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Seventh Joint Army-Navy-Air Force

Conference on

ELASTOMER RESEARCH
AND DEVELOPMENT

October 22 - 24, 1962

Office of Naval Research
Department of the Navy
Washington, D.C.

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ELASTOMER RESEARCH

AND DEVELOPMENT

October 22 - 24, 1962

Held at

U.S. Naval Radiological Defense Laboratory
San Francisco, California

Sponsored by
Office of Naval Research

Office of Naval Research
Department of the Navy
Washington, D.C.

FOREWORD

The Joint Army-Navy-Air Force Conference has met under rotating sponsorship at approximately two-year intervals as a continuing program of coordination. Need for this conference is based on a periodic re-examination of the intervening scientific and technical progress in the field and an appraisal of future critical weapons and systems requirements.

The published Proceedings taken together over the years provide the most complete available reference to the widely scattered military research and development program in elastomers and related materials.

Since the last meeting at Boston in 1960 sponsored by the U. S. Army Quartermaster Corps, substantial progress in several areas has been achieved in many laboratories sponsored by military agencies. New emphasis has been placed on the difficult problems arising from the new missile systems, the efforts to master penetration of outer space, the demands of high performance airplanes, the deep undersea environment and the tropical and polar land environments. Progress continues, but the residue of problems requiring solution remains large and diverse. It is important that scientists and technologists exchange knowledge and work for the fruitful "couples" through which accomplishment is facilitated.

Some additional coordination is provided with other agencies conducting related programs by allotting agenda space in the first session of the conference to program statements from their representatives. Our British colleagues, who sponsor important work in this field, have been invited to present similar statements; and we are happy to have their representatives here to tell of their programs covering the land, sea and air environments.

Attendance at this conference is by invitation only, and selection has been made to assure a maximum of contribution both here and in private programs by industry, research institutes, universities and individuals.

RADM L. D. COATES
Chief of Naval Research

iii

CONTENTS

(Pages 1 through 276 appear in Volume 1, Pages 277 through 498 appear in Volume 2)

Volume 1

SESSION I
OPENING REMARKS

SESSION II
ELASTOMER PROBLEMS IN MISSILE SYSTEMS

SESSION III
ELASTOMER PROBLEMS IN OUTER SPACE

Volume 2

SESSION IV
NEW POLYMERS OF ELASTOMER INTEREST

SESSION V
UNDERLYING SCIENCE AND APPLICATIONS

The titles of certain abstracts in these volumes are identified by (C). These titles
and abstracts are unclassified; however the original papers were Confidential and are
printed in their entirety in the Confidential volume which is being issued on a need-
to-know basis.

INTRODUCTION TO THE PROCEEDINGS

J. H. Faull, Jr.

Office of Naval Research

General Chairman

Over two hundred scientists and technologists assembled in
San Francisco for the 7th Joint Army-Navy-Air Force Elastomer
Conference. Reference to the paper titles reveals at once that
while the common denominator was that of polymer materials research
and development for weapons progress, the subject matter ranged
over a number of programs otherwise unrelated. The scientists
and engineers participating in this conference series meet elsewhere
in a variety of more specialized meetings called for other reasons
such as program guidance, contract review, state-of-the-art
definition and public disclosure. Here, however, is a unique
opportunity for information exchange and personal contact once
every two years between programs and people concerned with all
aspects of elastomer problems of military consequence. Of necessity,
some of the work and deliberations have first appeared elsewhere.

Traditionally, the opening session of this conference series
has included policy statements from the sponsoring service. These
have been reproduced in the Proceedings. Similarly, program reports
from the British services and other U. S. Government agencies, not
otherwise participating with technical papers, have been included.
For the first time anywhere, the comprehensive polymer program
of the National Aeronautics and Space Administration has been
outlined and is herein reproduced. This report should be a parti-
cularly valuable document for current coordination of military
programs.

New concepts of the molecular basis for elastomeric and other
viscoelastic behavior were presented by Professor P. J. Flory in
his opening remarks. The importance of such theoretical develop-
ments was reflected throughout the conference as, for example, in

the paper on "Crystallinity in Solid Propellant Binders" and on
"Performance of Compliant Skins in Contact with High Velocity Flow
in Water." Important additional molecular and viscoelastic theory
developments were reported in two later papers, "Molecular Structure
and the Mechanical Properties of Polymeric Materials" and "Comparison
of the Large Deformation and Ultimate Tensile Properties of Unfilled
Elastomers."

Discussion at this conference was stimulated after each major
topic presentation by statements prepared in advance based on the
early availability of a complete collection of abstracts. In
addition, all manuscripts had been submitted at least two weeks
prior to the meeting. A number of the prepared discussion state-
ments are included in the Proceedings in the order of presentation.
In many cases important discussions had to be curtailed for lack
of time. Under the topic concerning missile systems, spontaneous
discussion on rocket insulation revealed that more progress may
be expected in this area than has recently been reported. Discussion
on low friction rubber, important for a variety of dynamic seal
applications including those of outer space, revealed the importance
of unsolved controversial problems in this area.

At this conference, less attention was paid to antirads than
usual; although the interesting prospect has been brought to light
that some of the newer polymers and elastomers in prospect may
provide greater radiation resistance than any previously known
polymers. A single session of the conference was devoted to new
polymers of elastomer interest, although the lively discussion
following each subtopic indicated that more time would have been
well justified. Progress continues to be made in the measurement
and understanding of thermal degradation, more extensively treated
in several recent conferences and more directly devoted to this
subject. Two papers and extended additional discussion on boron
polymers clearly justified the hopes of two years ago that diver-
sion of research effort from that of boron-high energy fuels to
boron polymers would lead to the discovery of important high
temperature resistant and other polymers and elastomers; all of
the details are, for the present, confined to the classified
supplement of this Proceedings. Other hetero-atom chain polymers
are not without promise and discussion revealed continuing
confidence for discovery of useful high temperature resistant
carbon chain elastomers. Noteworthy progress was reported for the
stubborn fluorocarbons, particularly the hope that at last linear
perfluoroalkyltriazines may be synthesized with maybe 200°F
higher temperature resistance than the best commercially available
fluoroelastomers.

In addition to the theoretical importance of the final session,
already mentioned, two applications were discussed in which

functional elastomeric coatings are under investigation. In the case of underwater protection of surfaces against cavitation, substantial progress was reported towards an operational status. In the case of compliant skins for increasing the velocity of underwater vehicles, much more is now known about the nature of problem elements requiring solution. The most serious problem is the heretofore unrecognized "static divergence" phenomenon which may set the upper velocity limit achievable but may also contribute to the understanding of cavitation protection failure.

It is felt that this conference was particularly informative and satisfying to those in attendance. Success was due in large measure to the excellently prepared and presented papers. Their value was enhanced by much more discussion than usual which was stimulated by discussion leaders who offered some thoughtfully prepared comments and augmentations. Unfortunately, time prevented reporting of important prepared discussion as well as inclusion among the formal papers new findings of important research. Nevertheless, this was a highly successful conference from which important "coupling" results can be expected between materials research and development on the one hand and weapons advance on the other.

In this unclassified section of the Proceedings, unclassified abstracts of classified papers are included.

ACKNOWLEDGEMENTS:

In addition to the authors themselves, grateful acknowledgement for willing cooperation is extended to the government laboratories concerned and to the many military contractors entrusted with the research and development progress reported at this conference. The excellent support and participation from the British Admiralty, the British Ministry of Aviation and the Canadian Defense Research Board is particularly appreciated. Contributions from the office of the Director of Defense for Research and Engineering, the office of the Assistant Secretary of the Navy for Research and Development and the National Aeronautics and Space Administration were invaluable.

Naval activities which provided facilities, personnel support and logistics included first of all the Navy Radiological Defense Laboratory but also the San Francisco Naval Shipyard, the Mare Island Naval Shipyard and the San Francisco Branch Office of Naval Research.

Members of the Planning Committee who gave extensively and generously of their time include C. B. Griffis of the U. S. Army, J. M. Kelble of the U. S. Air Force, E. Bukzin of the Bureau of Ships, J. J. Gurtowski of the Bureau of Naval Weapons and their

associates. R. E. Wiley of Code 104, Office of Naval Research,
Washington, provided an essential service as secretary to the con-
ference. I. Rudin of the Technical Information Division, Naval
Research Laboratory, directed the work required to issue these
Proceedings.

Washington, D. C.
January 1963

Session I

OPENING REMARKS

Chairman: J. H. Faull, Jr.
U.S. Navy

NAVY'S PROGRAM ON MATERIALS

H. J. White, Jr.
Office of the Assistant Secretary of the Navy (R&D)
Washington, D. C.

Mr. Chairman, honored guests and fellow participants in the Seventh Joint Army-Navy-Air Force Conference on Elastomer Research and Development.

Dr. Wakelin, the Assistant Secretary of the Navy for Research and Development, has asked me to convey to you his hopes for the success of this conference and his regrets that the pressures of the Navy's research and development business keep him from being present today. As several of you know, Dr. Wakelin has maintained an active interest in elastomer research throughout his career. In addition to bringing Dr. Wakelin's greetings, I am going to outline briefly that portion of the Navy's program on materials which is concerned with polymers. Perhaps my remarks will add some perspective to the Navy contributions to the conference.

Probably it would be more precise to refer to Navy programs, since there are several groups in the offices and bureaus of the Navy with responsibility for research and development activities involving polymeric materials. Although these groups are essentially independent, their efforts are closely coordinated through the Navy Advisory Council on Materials which, of course, is concerned with nonpolymeric materials as well.

General Considerations

Many of the bureaus and offices, which are the producers and service organizations of the Navy, have interests in polymeric materials and have programs to solve various pertinent problems. Most of the problems fall under the purview of the Bureau of Naval

Weapons, the Bureau of Ships, or the Office of Naval Research. The interests of the Bureau of Naval Weapons and the Bureau of Ships in materials are too varied to enumerate easily; the Office of Naval Research, as the name implies, has a general responsibility for research in areas of importance to the Navy. In addition, the Bureau of Yards and Docks is interested in the protection of docks and other shore structures from the corrosive effects of sea water and the seaside atmosphere; the Bureau of Supplies and Accounts is concerned with clothing, especially protective clothing of various types, and packaging; the Bureau of Medicine and Surgery with prosthetic devices; the Oceanographic Office with charts; and the Marine Corps with a variety of specific applications.

If we break away from the organizational structure of the Navy and consider what improvements in inherent characteristics are needed to solve the various problems mentioned, several categories can be listed.

First, and probably foremost, is the need for improved mechanical properties. Higher tensile strength and / or initial modulus are usually desired especially for rigid materials; various dynamic properties are often important with elastomers. Temperature is an important parameter here with the need for improvement greatest in the higher temperature ranges.

Another need is for materials which retain initially acceptable mechanical properties under a variety of conditions such as the presence of light and other forms of radiation; of corrosive fumes; of gases, such as oxygen; of liquids, such as hydraulic fluids which may be corrosive or cause swelling; and of sea water. Changes with time are of primary importance, since what constitutes an acceptable useable lifetime varies markedly with the nature of the proposed use.

There are also a variety of special environmental problems. For example, polymers for use in closed spaces such as submarines or space capsules must meet special criteria. Presence of small amounts of solvent, plasticizer, or monomer which would be inconsequential for most uses may constitute an important health hazard. Similar trace quantities could result in adhesional or other failures under high vacuum. Anechoic coatings and coatings for protection against cavitation are other special problems.

2

Specific Programs

To provide a bit more focus to the discussion, I will mention certain specific programs briefly.

The effort to obtain plastics, elastomers, and oils of suitable stability at higher temperatures, has led to a widespread study of the possibilities inherent in polymers without carbon backbone chains. The areas investigated include phosphorus/nitrogen polymers, boron compounds and silicon polymers. Unusually stable organic polymers are also being studied for specific uses. The results of several of these studies are on the program of this conference.

Another area of considerable activity is the field of laminates. In addition to the search for resins having higher thermal stability and for solutions to adhesion problems, a variety of fillers are being studied. These include hollow glass fibers, which offer certain advantages where pressure vessels are concerned, metal-coated glass fibers, silica and ceramic fibers and chips, and composite structures which include metallic foils for enhanced mechanical properties. Resin laminates offer attractive possibilities for the hulls of deep-diving submarines; however, additional information is required on the creep and fatigue properties, and on susceptibility to attack by sea water. Design information is also needed because of the marked differences of properties between laminates and more conventional hull materials.

Polymer foams are used in structural members to provide buoyancy, strength, and to spread loads. An example is their use in the diving planes of submarines. They are also used for electrical or thermal insulation and for filling unwanted cavities. At present, water logging can become a problem and various solutions are being investigated.

In addition to studies of coatings for protection against cavitation and anechoic coatings, which have already been mentioned, coating for protection against corrosion, for damping to reduce fatigue effects and to provide lubrication are also being investigated at the present time.

Another form of environmental problem, which has not been mentioned, is the development of seals which are effective for larger differences in pressure than are now useable. These seals would be useful for deep submergence and for retaining gases or

3

hydraulic fluids under higher pressures.

Finally, there are several physical and chemical studies involving solid propellants. Basic studies are being carried out on the mechanism of the thermal degradation and combustion of polymers, both in filled and in hybrid systems, and polymers which undergo exothermic or endothermic decomposition. Other work of interest involves the rheology of propellants and effects of storage.

Trends

In closing, I might mention certain trends which are becoming apparent.

As the number of polymers containing other than the conventional carbon backbone increases, there will be increased activity in the evaluation of these polymers. Hopefully, this will lead beyond the polymer-by-polymer investigation of properties and make clear relationships between chemistry and properties, such as now exist in organic chemistry, which will, in turn, lead to further more directly oriented work on synthetic methods.

There should also be a concomitant rise in the study of reactions and changes in the solid state. Such studies are obviously a necessary part of any determination of stability and are being hastened along as different nondestructive tests are developed. A recent development in one of the Navy's laboratories is a continuous-current-monitoring device which provides a sensitive measure of resistance. Since resistivity is altered by various physical and chemical changes within a polymer, such a device provides another nondestructive method of following changes occurring in the solid phase.

Last, but not least, the correlation of the physical and chemical properties of materials must be accompanied by a more subtle and rigorous analysis of the properties required of materials for various uses, so that effort may be expended in areas of need and high probability of success.

INTRODUCTORY REMARKS

Captain F. D. Kellogg, USN

Commanding Officer

ONR San Francisco

In 1946 Congress established the Office of Naval Research to plan, foster and encourage scientific research in recognition of its paramount importance as related to the maintenance of future Navy power and the preservation of national security.

To discharge a responsibility of this magnitude requires that the Office of Naval Research do much more than conduct a research program. Frontiers of scientific areas vital to the Navy must be intensively pushed forward. Results of research must be made available to developmental agencies of the three services and industry.

About 80% of the Office of Naval Research research program is conducted by contracts with universities, non-profit organizations, and researchers in private industry. This program is supported and administered by the Research Group in Washington, D.C. In addition, the Naval Analysis Group conducts broad systems and warfare studies. Branch Offices located in major cities in the continental United States assist in administering the program and maintaining liaison with the local scientific communities. A branch office is located in London, responsible for making similar contacts in Great Britain and Europe.

The Office of Naval Research conducts research in its in-house laboratories, particularly in fields requiring extensive Navy experience in support of specific Navy facilities. Through the Research Coordinator and the Development Coordinator in Washington, D. C., the Office of Naval Research integrates the many research and development programs of the bureaus of the Navy, the Armed Services, and the Office of Naval Research.

For the past twelve years the tri-service Elastomer Conference has met biannually under rotating sponsorship of the Army, Navy and Air Force. The purpose of this conference is to provide the scientists and engineers of the three services the opportunity to examine, in conference, the intervening scientific and technical progress made in the field of elastomers, and to afford a coordinated means of tri-service appraisal of the progress in research and development for future weapons and weapons systems.

Since the last meeting in Boston, in 1960, hosted by the U. S. Army Quartermaster Corps, substantial progress has occurred in the areas of high and low temperature resistant elastomers; radiation-resistant elastomers; mechanism of polymer degradation; correlation of mechanical properties with molecular structure; and synthesis of novel polymer types.

New emphasis in the Office of Naval Research program has been placed on research in the field of inorganic coordination polymers and polymers based on boron, with a view toward novel thermally stable polymer systems resistant to temperatures of $1000^{\circ}F$.

The three services have expended much effort to master penetration of outer space, to develop new high-performance airplanes, to obtain more knowledge about the inner spaces of the deep sea environment, the tropical climate and the polar land environments. Progress is being made in all of these areas, but the residue of problems requiring solution continues to be large and diverse. For instance, retention of mechanical properties at high and low temperatures, prevention of deterioration by solvents (including rocket fuels and oxidizers), prevention of deterioration by nuclear and solar radiation and improvement of properties by appropriate compounding, blending and curing techniques.

These conferences have provided the scientists and technologists of the tri-service and other military agencies the opportunity to exchange knowledge, and to work toward accomplishment of solutions to many of these problems through a joint effort. In addition, by invitation to this conference distinguished scientists from the Office of the Assistant Secretary of Defense for R&D, other governmental agencies, and our British allies, have been afforded the opportunity to present progress of their programs covering the land, sea and air environments. Contribution to these conferences has also been afforded the private programs sponsored by industry, research institutes, universities and qualified scientists.

On behalf of Admiral Coates, the Chief of the Office of Naval Research, it gives me great pleasure to welcome you to the Seventh tri-service meeting on Elastomer Research and Development.

INTRODUCTORY REMARKS

Dr. Earl T. Hayes

Special Assistant for Materials

Office of the Director of Defense Research and Engineering

I would like to tell you briefly today of the place of chemistry and materials in the Office of the Director of Defense Research and Engineering and to emphasize the degree of technical representation at this level that now exists. Everyone at the working level professes a desire to know what's going on at the top level of any organization or how things operate in Washington. Yet, if a piece of paper describing such operations comes down through the regular channels, it is rarely read or studied. I honestly don't know whether this comes from the fact that organizations have proliferated to such an extent that the organization charts have become meaningless or whether the administrative people are trying to match the technical people in doubling their output of literature every seven years. Seriously, though, I believe you would like to hear about some of the functions of our office and an idea of what we intend to accomplish during the next year.

The Deputy Director for Engineering and Chemistry, under Dr. Harold Brown, is Dr. James H. Gardner on leave from his post of General Manager of the National Research Corporation. Under the structure set up early this year, Dr. Gardner has complete responsibility at the DOD level for research and development activities of the military in chemistry and materials. I assumed the position of Special Assistant for Materials under Dr. Gardner in May of this year.

As Assistant Director for Chemical Technology, Dr. Gardner has appointed Dr. Jack Thurston, formerly Director of the Stamford Laboratories of American Cyanamid and a top flight organic chemist. Dr. Thurston has primary responsibility for biological and chemical warfare, fuels including propulsion, oils and lubricants. Although

Dr. Gardner came from a metals development project to his current position, he was trained as an organic chemist and worked in the petrochemical industries. It cannot be said that everyone in the organization is an organic chemist because I am fundamentally metals and nonmetallic materials oriented.

The importance of materials of all classes to the Defense effort has been recognized in the establishment of a separate office devoted only to this purpose. Materials development programs support all areas of weapon and equipment development whether it be ordnance, aerospace vehicles, missiles, submarines or electronics. Aside from electronics, it is certainly the largest area of applied research and a most important part of the defense program. The results of materials research are not confined to a specific project but are capable of universal application.

I would like to dwell on the subject of the total materials effort and its importance in our planning activities. First, let me say that no one knows how much is spent on materials research and development in this country. We can identify $80 to 100 million of direct appropriations in our office but estimate this is only about a quarter of the total effort. Practically all systems contracts permit the contractor to spend up to 5% on research associated with the program. In addition, the contractor has considerable latitude in development activity in order to guarantee the reliability and performance of the complete system and associated vehicles. There is every reason to believe that the amount of money spent on materials development in system contracts involving large vehicles exceeds what would have been necessary with a planned research and development that had anticipated the broad materials needs of the Services. No one has ever truly identified the amount spent on materials research and development under these end item contracts.

For several years there has been a requirement on most RDT&E contracts and systems contracts that materials research results be reported as separate financial and technical items. Actually, little or nothing has been done about this clause in the contracts and, to this day, most of the research done with hardware money is unrecorded and uncoordinated. In the near future we will be asking the Services and contractors to give us an assessment of the current materials research effort all the way from fundamental research through the development stages up to final production.

You all know that, as you move up the R&D scale from basic research to end item development, the cost of doing research or development multiplies by a factor of 5 to 10. Knowledge builds on knowledge and each step of an orderly development is a logical consequence of knowledge gained at a preceding level of research.

Once we have obtained an idea of the total materials effort of the country, we can arrive at some conclusions as to whether or not the materials work and its contribution to the development of weapons might be cheaper and more effective under an expanded materials effort in the research and exploratory development phases.

In other office activities, we have reviewed a number of specific materials programs and found that the area of composites is one of the most promising fields of development at the present time. As an example in this area, plastic reinforced glass fiber structures have doubled in strength in the last three years and it can be predicted that they will double again in the next three years. This is truly a remarkable performance compared to the incremental increases that the metals people gain by alloying procedures. In fact, one could say that this development alone is a breakthrough in every sense of the word and should be recognized as such. The amount of research being done on fiberglas composites alone is bound to have a remarkable effect on research concerned with chemistry and physics of surfaces, chemical binding and wetting, mechanics of design with brittle materials and will produce a marked industrial development before too many years in the organics-composite field. For a close examination of this particular field, we are asking our technical advisory group, the Materials Advisory Board, to augment its staff with people of competence in this area.

We work very closely with the Services in their operation of material information centers. The Defense Materials Information Center, funded by the Air Force and located at Battelle Memorial Institute, and Plastec, funded and operated by the Army at Picatinny Arsenal have been of great help in the metals and plastics areas, respectively. We exercise a coordinating function here to insure maximum use of the potential of these activities.

We are well aware of the importance of elastomers in the materials picture and stand ready to assist you in any way in coordinating your R&D programs. This really is an empty sentence because you have in this joint Army, Navy and Air Force conference, the finest type of cooperation that we could expect. Finally, I searched vainly for some morsel of technical information that would show my knowledge in this area. I reviewed the notes of our various materials briefings and came to the rather morbid conclusion that you gentlemen are faced with the seemingly impossible task of producing materials which will remain plastic from 400° below zero to $3,000^\circ$, maintaining, of course, all the favorable physical properties without chemical deterioration. It can only be said that this is the problem faced by the whole materials community. In the process of attempting to meet what, at the outset, seem to be hopeless demands, we find that we do produce something much better than we even dreamed of a decade before.

POLYMER RESEARCH IN THE NATIONAL AERONAUTICS & SPACE ADMINISTRATION

B. G. Achhammer

Office of Advanced Research and Technology

Washington, D.C.

It is my understanding from Dr. Faull that this represents
the first appearance, at least officially, of the NASA at a JANAF
Elastomer conference. First then let me express my thanks on
behalf of NASA, particularly myself and the scientists from several
of our research centers, namely Langley, Ames, Marshall and the
Jet Propulsion Laboratory, for the opportunity to attend this
seventh session of your conference. Judging by your past conferences
this should be a stimulating and productive meeting on a subject
which is of increasing importance to NASA.

Following Dr. Faull's suggestion the primary objective of
this presentation will be to acquaint you with the NASA organization,
specifically with respect to polymer activity, and to provide you
with some idea of our current polymer program with emphasis on
elastomers. The NASA organization shown in Figure 1 consists of a
Headquarters operation and seven research centers. No attempt
has been made to detail this structure since it is not pertinent
to our objective. Likewise, the launch facilities and other aero-
nautical capabilities are omitted. Immediately below the Admini-
strator's office is the Associate Administrator who, it will be
observed, has a direct line of authority to the four Headquarters
offices and to each of the Research Centers.

The headquarters operation consists of four technical offices:
(1) The Office of Applications which is primarily responsible for
the utilization of space to the benefit of the people generally
by such ventures as weather forecasting and communications, and
secondarily is responsible for ferreting out advances in technology
throughout NASA and bringing them to the attention of producers of
purely civilian devices; (2) the Office of Space Sciences which is

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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OFFICE OF
MANNED SPACE FLIGHT
D.B. HOLMES

OFFICE OF ADVANCED
RESEARCH & TECHNOLOGY
R.A. BISPLINGHOFF

AMES
RESEARCH
CENTER
MOFFETT
FIELD, CALIF.

GODDARD
SPACE FLIGHT
CENTER
GREENBELT,
M.D.

JET PROPULSION
LABORATORY
(CONTRACTOR
OPERATED)
PASADENA, CALIF.

LANGLEY
RESEARCH
CENTER
HAMPTON,
VA.

LEWIS
RESEARCH
CENTER
CLEVELAND,
OHIO

MANNED
SPACECRAFT
CENTER
HOUSTON,
TEXAS

GEORGE C.
MARSHALL
SPACE FLIGHT
CENTER
HUNTSVILLE, ALA.

Figure 1

11

responsible for unmanned scientific investigations of space, the
moon and the planets and controls Surveyor, Ranger, Mariner, the
Orbiting Geophysical Observatory, Orbiting Solar and Astronomical
Observatory satellites, and all sounding rocket programs; (3) the
Office of Manned Space Flight which is responsible for overall
systems engineering and evaluation for the various manned space
flight projects, such as Mercury, Apollo, and Gemini including the
spacecraft, all launch vehicles of the Saturn and above classes,
ground support equipment, tracking stations and communications
network; and (4) the Office of Advanced Research and Technology
whose function it is to plan and conduct research and advanced
technological studies to guide, support and show feasibility for
future space activities. The Office of Advanced Research and
Technology also has responsibility for the development of nuclear
rockets and auxillary power generators.

The organizational structure of OART is shown in Figure 2.
The Materials Research Program which is under the Research Director-
ate is responsible for management and coordination of all non-end-
item oriented research within the NASA complex. Materials research
directly related to an operating system, such as Apollo or OGO, is
under direct management of the Headquarters Office or the NASA
Research Center to which it is assigned. In addition the Materials
Research Program headed by George C. Deutsch is concerned with
long-range research and technological studies which may be of value
to any of the other Headquarters offices or any of the research
centers. The Materials Research Program includes advanced studies
on ceramics, metals, solid state physics, materials for supersonic
transport, and polymers.

The NASA was created, as you undoubtedly know, September 30,
1958. The National Advisory Committee for Aeronautics, including
the Research Centers at Ames, Lewis and Langley and other aero-
nautical facilities, Dr. Wehrner Von Braun's group of the Army
Ballistics Missile Agency, and the Jet Propulsion Laboratory were
brought together to form the nucleus for the NASA complex.

From a materials point of view the National Advisory Committee
for Aeronautics was oriented primarily toward aeronautics and, as
a consequence, its primary materials program was concerned largely
with high temperature materials. With the advent of the space age
and its exotic new environments and requirements, the materials
needs grew. The inability of metals to withstand re-entry and the
fact that polymers provide a means of re-entry through ablation
phenomena, the needs for high strength to weight ratio materials,
and apparent advantages of inflatable structures expanded the
interest in polymeric materials.

12

Figure 2

OFFICE OF
ADVANCED RESEARCH AND TECHNOLOGY
R.A. BISPLINGHOFF

PROGRAM REVIEW & RESOURCES MANAGEMENT
B. MEYERS

AERONAUTICAL RESEARCH
C.H. ZIMMERMAN

SPACE VEHICLES
M. AMES

NUCLEAR SYSTEMS
H. FINGER

RESEARCH
H.H. KURZWEG

BIOTECHNOLOGY & HUMAN RESEARCH
E. KONECCI

ELECTRONICS & CONTROL
A.J. KELLY

CHEM. PROPULSION & POWER GENERATION
J. SLOOP

SPACE NUCLEAR PROPULSION OFFICE
H. FINGER
GERMANTOWN MD.

PHYSICS OF FLUIDS
A. GESSOW

ELECTRO-PHYSICS
H. HARRISON

MATERIALS
G.C. DEUTSCH

APPLIED MATHEMATICS
R. WILSON

In any case, NASA polymer interests are of relatively recent origin; and, consequently, we are discussing a developing picture rather than a mature or rigid organization and program. Studies involving polymers are conducted in each of the NASA research centers and reflect in most cases the specific needs and requirements of the respective Center. These studies are concerned, in general, with (1) evaluation of polymers for specific application; and (2) engineering design for polymers. Activity of this type which is primarily applications oriented is scattered throughout the various centers. It follows that the bulk of such work is carried out by engineers and scientists who are not oriented to polymers as such.

For example, the Lewis Research Center located at Cleveland, Ohio, concentrates on research relative to propulsion and power generation for space vehicles. The need for tanks operating at cryogenic temperatures has naturally led this center into evaluation studies on filament-wound devices, polymeric liners, expulsion bladders, seals, sealants and lubricants. Of specific interest is gas permeability at cryogenic temperatures. The entire effort here is relatively small with respect to polymers. Polymer research, as such, is not conducted at the Lewis Research Center. Some consideration is being given, however, to initiating studies on reactions of polymers at ultra-high pressures.

The Ames Research Center, located at Palo Alto, California, is concerned with gas dynamics research at extreme speeds, automatic stabilization, guidance and control of space and re-entry vehicles, and to space environmental physics. It is also the NASA research center for studies in the life sciences. Polymer activity is being initiated in two major areas: (1) ablation phenomena; and (2) space environmental effects. The ablation studies will be primarily devoted to explaining the mechanism of ablation rather than screening tests for materials. Space environmental effects, including vacuum, electromagnetic radiation, particulate radiation, and micrometeoroid impact will be studied as a composite environment. These are currently developing programs in which polymers will be evaluated and studied; but, again, the emphasis of the programs is not necessarily on polymers per se.

The Goddard Space Flight Center, located at Greenbelt, Maryland, is responsible for scientific satellites, sounding rockets, and tracking and data systems. Polymer activity reflects this Center's objectives through research and development studies on the chemistry and physics of non-metallic surface coatings and evaluation studies on adhesives, potting compounds and encapsulants. The evolution of more accurate and more economical testing techniques is also of interest at the Goddard Center.

The Manned Spacecraft Center, the newest NASA center which is being constructed at Houston, Texas, is responsible for manned space flights including the remain g Mercury program, the Apollo program and the Gemini program. The only discernable polymer activity at the present time is of an indirect nature related to evaluation and development of heat shields. Polymer research and development studies on a broader scope will undoubtedly be undertaken in the future.

The George C. Marshall Space Flight Center at Huntsville, Alabama, is concerned with the development of advanced launch vehicles, such as Saturn. This Center conducts a relatively large contract program involving polymers because of specific requirements for sealants, adhesives, gasket materials, etc. In-house research in polymers is also carried out at the Marshall Center in areas aligned with its objectives. Marshall's activities in polymers are directed, perhaps more so than any other NASA Center, toward elastomers and this aspect of their work will be described in more detail later in this discussion.

The Langley Research Center situated at Hampton, Virginia, conducts research on structures and material applications, the aerodynamics of re-entry vehicles, continuing work in aircraft aerodynamics and structures, and fundamental research in plasma physics. The polymer program at the Langley Research Center involves both basic and applied research problems. The structures research work at Langley naturally envelopes new materials. Consequently, polymers are being evaluated and engineering design criteria established for applications such as ablators, foamed structures, filament-wound motor cases and space stations.

The Spacecraft Materials Section of the Space Vehicle Branch of the Langley Center was authorized to establish a basic polymer laboratory in 1961. The organization of this laboratory is shown in Figure 3 which also defines the areas in which studies are being made. The objectives of the basic polymer laboratory include the developing of basic information on the properties and limitations of polymers in space environments; a unified approach to polymer chemistry and physics; and, acting as a central in-house source of basic information on polymers for the various research and development groups using polymeric materials within NASA. As the organizational chart shows this group is concerned with molecular properties of polymers, viscoelastic properties with emphasis on prediction of structural properties changes due to space environment, composite materials and basic studies on thermal control surfaces. This group which is a nucleus for basic polymer studies in the NASA complex has a staff of five professional scientists under the leardership of Dr. George F. Pezdirtz. It is anticipated that this group will continue to grow as a valuable NASA in-house capability.
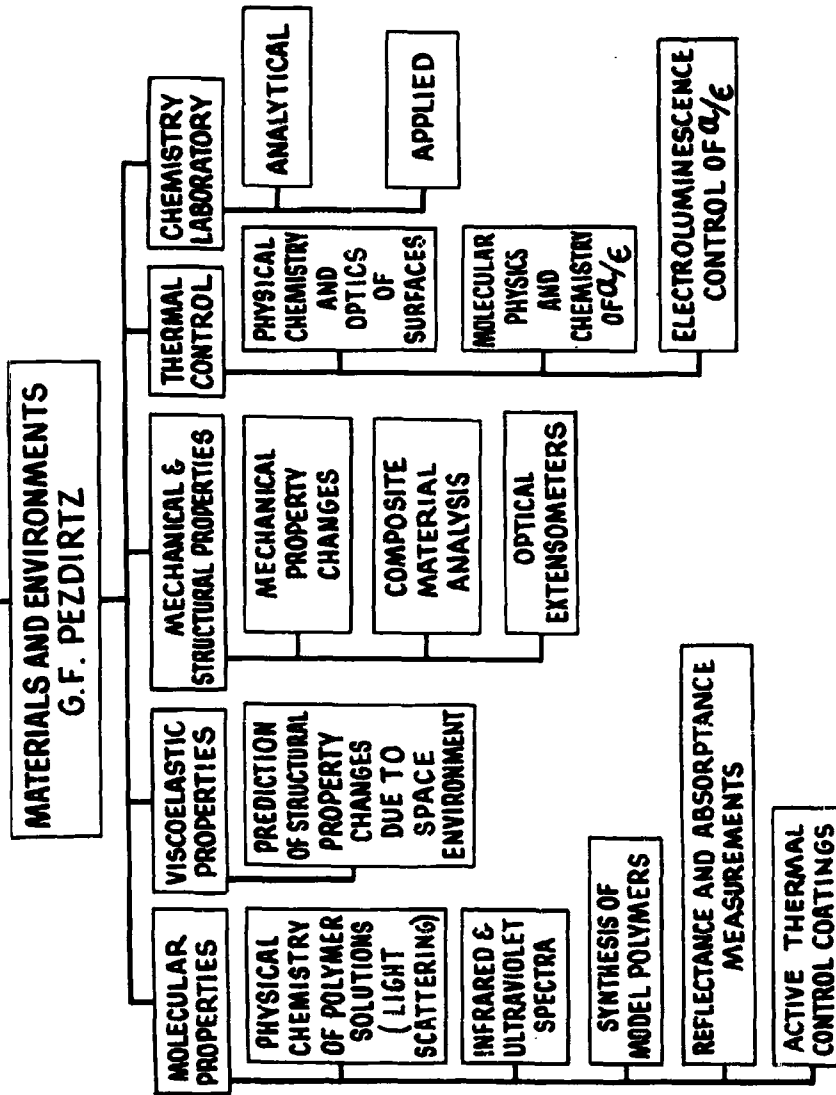
Figure 3

Another basic polymer capability in the NASA complex is at the
Jet Propulsion Laboratory. Strictly speaking, JPL is not a NASA
center since it is operated on a contract basis for the NASA by the
California Institute of Technology to conduct studies concerned
with the exploration of deep space with interim responsibility
for early lunar exploration; however, in program and budget
considerations JPL is considered in the same light as the NASA
research centers. The polymer research activities conducted in
the Polymer Research Section under Dr. Robert F. Landell are a
portion of the overall undirected research effort of JPL. The
organization chart for this section is shown in Figure 4. Basic
polymer studies involve viscoelastic behavior, electrical conduc-
tivity in terms of the mechanism of electronic energy transfer,
high temperature stability, glassy transition phenomena and degrada-
tion mechanisms. As this figure shows the work of this group is
supported in part by ARPA funds.

More directed studies, involving polymer degradation under high
heat flux and degradation in vacuum, are carried out in another
section at JPL. Applied polymer studies such as application of
polymers to hardware, effects of space environment on temperature-
control surfaces, and studies concerned with selection of high
energy radiation resistant materials for spacecraft and selection
of heat shields for planetary entry capsules are conducted in
other parts of the JPL organization.

The elastomer studies in the NASA follow the same pattern as
the general polymer activity. Each center in conducting studies
oriented to its specific problems and requirements involves
materials which, in the broad sense of the word, are elastomers.
In this respect, polyurethanes for propellant systems, butyl
shells for space stations, and even some ablation systems can be
considered elastomer studies. In fact, Dr. Faull is, I understand,
currently working on the problem of defining an elastomer and, in
his opinion, polymers in these applications are elastomers.

As one observes the polymer activity within NASA, however,
two laboratories are distinctly more concerned with elastomeric
materials, per se, than the others. These two are the Marshall
Space Flight Center and the Jet Propulsion Laboratory. Figure 5
lists some of the Marshall activities in this area under the
direction of Dr. William Lucas. Elastomer projects range from
aging evaluation, through development, to synthesis of polymers
with potential elastomeric properties. In-house effort at
Marshall is augmented by a substantial contract program.

The Marshall Space Flight Center's program on the synthesis
and characterization of a class of polymers identified as silazanes
may be of specific interest since a paper on the synthesis of

17

Figure 4

JET PROPULSION LABORATORY

POLYMER RESEARCH SECTION
R.F. LANDEL

ARPA

NASA

POLYMER CHEMISTRY

PHYSICAL CHEMISTRY

RHEOLOGY

DEGRADATION MECHANISMS

NONDESTRUCTIVE TESTING
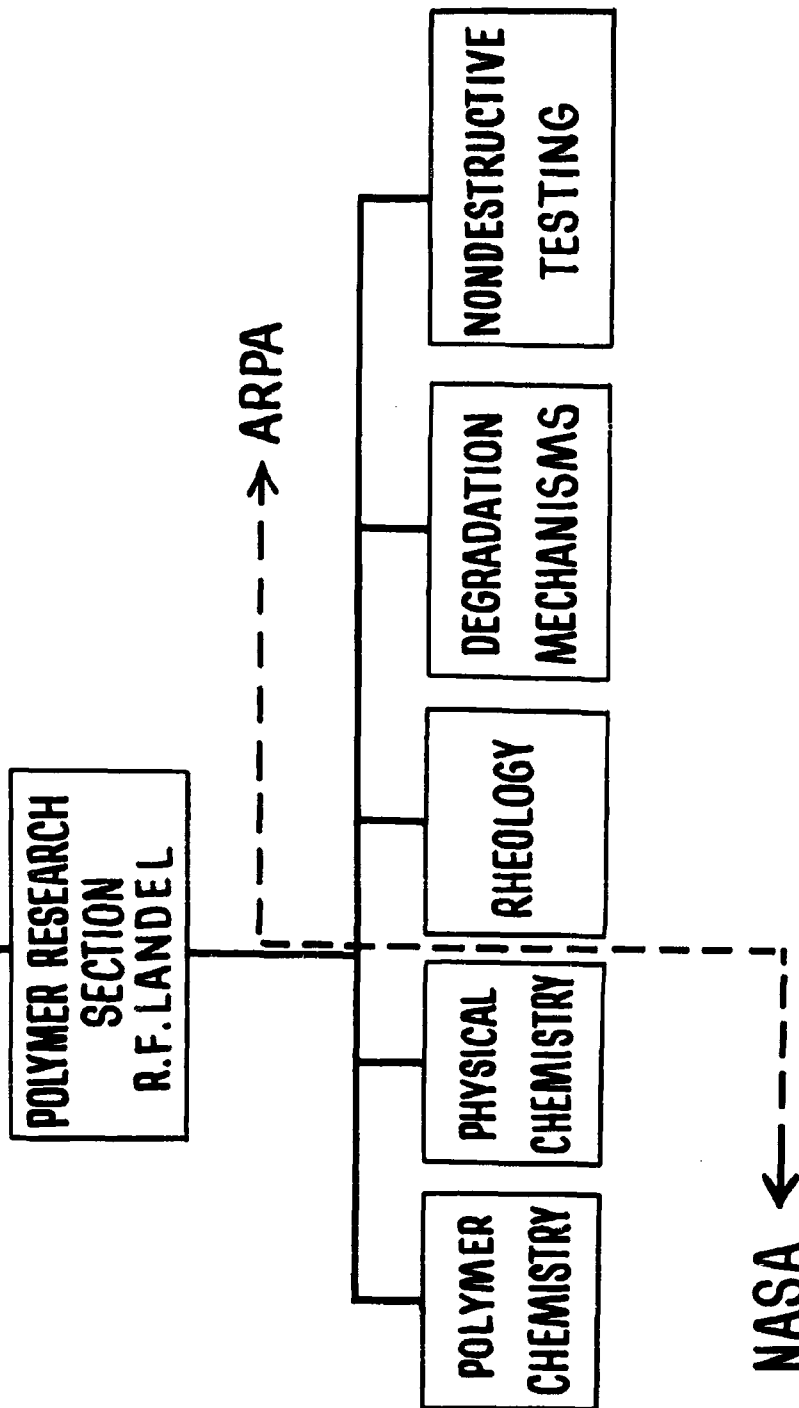
ELASTOMER STUDIES

GEORGE C. MARSHALL SPACE FLIGHT CENTER

1. AGE DETERIORATION OF GASKET MATERIALS

2. ENGINEERING, FABRICATION AND RELATED SERVICES ON RUBBER

3. DEVELOPMENT OF ORGANIC SEALANTS FOR APPLICATION AT VERY LOW TEMPERATURES

4. RESEARCH AND DEVELOPMENT OF IMPROVED GASKET MATERIALS FOR CRYOGENIC TEMPERATURES IN SPACE

5. COMBINED EFFECTS OF RADIATION AND VACUUM ON ELASTOMERS

6. POLYMERS CONTAINING Si-N BONDS

Figure 5

elastomers containing Si-N bonds in the main chain will be presented at this conference by L. W. Breed and R. L. Elliott of the Midwest Research Institute. The Marshall program in this area consists of both in-house research and supporting contract research. The contract research is being done at the Southern Research Institute at Birmingham, Alabama, and is a continuation of a program originally funded while this group was a part of the Army organization. This effort principally involves studies of silazane type compounds,
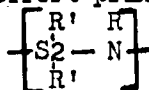
$$\left[\begin{array}{cc} R' & R \\ Si_2 - N \\ R' \end{array}\right]$$ shown in Figure 6. These compounds are prepared by

reacting halosilanes with ammonia or organic amines. They are generally characterized by their resistance to elevated temperatures.

Two routes to linear polymers have proven feasible. A direct route involves the reaction of difunctional silanes or silicon oxychlorides with organic diamines. Alternatively, polymers may be formed by the Lewis-acid catalyzed amine exchange reaction between simple or cyclic silazanes and organic diamines.

This work has shown that some silazanes can be converted by heating at $400^\circ C$ to $500^\circ C$ to complex condensation products of extraordinary thermal stability. The silazane made from ethylene-diamine by the reaction scheme shown in part b of Figure 6 can be converted to an elastomeric gum by heating in air at $350^\circ C$ to $400^\circ C$. This elastomeric material is resilient at $-78^\circ C$ and after heating at $450^\circ C$ for 0.5 hours.

This program is continuing at the Marshall Space Flight Center with emphasis being placed upon practical coatings and other high temperature applications of the silazanes. Other possible polymer intermediates containing silicon-nitrogen bonds are being investigated.

The JPL elastomer studies are concerned with crosslinked and non-crosslinked diisocyanate-linked elastomers containing substituted urea groups. Polymers are formed from diisocyanates and polyfunctional molecules containing active hydrogens or from the isocyanates themselves. These materials serve for basic studies on the relationships of physical properties to chemical structure, network topology, chain flexibility, and intermolecular forces in polymers. Figure 7 shows some of the basic elastomer problems of interest to this group.

I hope that I am leaving you with the impression that NASA is in the process of establishing in-house capability in polymers, including elastomers. It is recognized, however, that the research and technology required for NASA objectives cannot be accomplished on in-house effort alone. An increased contract program is

MARSHALL SPACE FLIGHT CENTER
Si-N POLYMERS

a)

$$\left[\begin{array}{c} R' \\ | \\ -Si- \\ | \\ R' \end{array} \begin{array}{c} R \\ | \\ N- \end{array} \right]$$

b) $\dfrac{x}{3}$ (CH$_3$)$_2$Si

$$\begin{array}{c} (CH_3)_2 \\ Si \\ HN \qquad NH \\ | \qquad\qquad | \\ Si(CH_3)_2 \\ \diagdown N \diagup \\ | \\ H \end{array}$$

$+ \ X \ H_2N{-}C_2H_4{-}NH_2 \xrightarrow[\;NH_4Cl, etc.\;]{(NH_4)_2SO_4}$

$$\left[\begin{array}{c} CH_3 \quad H \\ | \qquad | \\ Si{-}N{-}C_2H_4{-}N \\ | \qquad\qquad | \\ CH_3 \qquad H \end{array} \right] + X NH_3 \uparrow$$

Figure 6

21
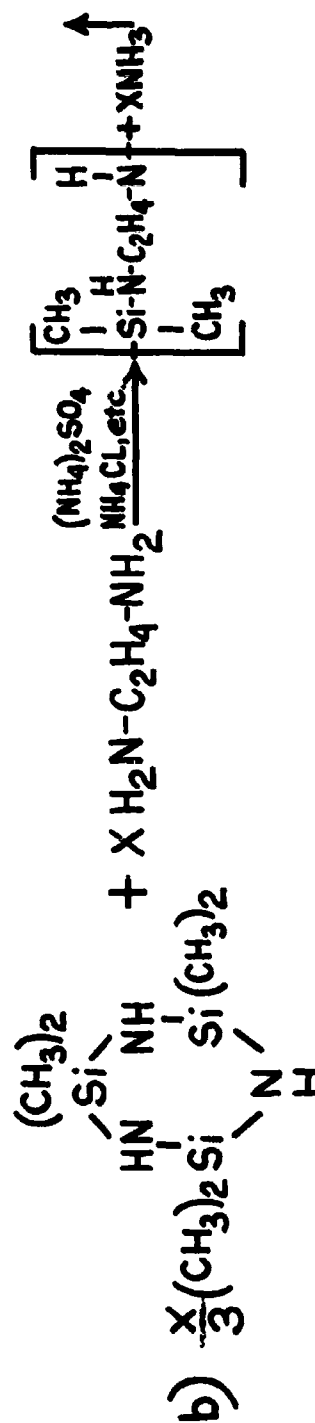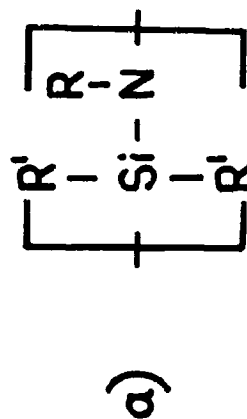
ELASTOMERS STUDIES
JET PROPULSION LABORATORY

1. SYNTHESIS OF CROSSLINKED AND NON-CROSSLINKED ELASTOMERS

2. TIME-DEPENDENT AND TIME-INDEPENDENT (EQUILIBRIUM) MECHANICAL PROPERTIES OF ELASTOMERS UNDER BOTH SMALL AND FINITE DEFORMATIONS

3. INTERRELATION OF CHEMICAL GROUP CONTENTS AND GLASS-TRANSITION TEMPERATURE OF ELASTOMERS

4. DIFFERENCES BETWEEN PROPERTIES OF ELASTOMERS WITH NETWORKS FORMED FROM EITHER INTERMOLECULAR OR COVALENT CHEMICAL BONDS

5. FRACTURE UNDER VARIOUS LOADING CONDITIONS

Figure 7

envisaged involving industry, research institutes, and the universities. Development of in-house competency, however, is recognized as a prerequisite for a well conducted and productive contract program, especially since the contract program will be largely center oriented. Contracting out of NASA Headquarters will be primarily devoted to basic studies on polymers and to exploration of new areas of polymer research. Some of the headquarters funds will, however, be used to support center oriented research.

In order to place this discussion in perspective, it should be observed, that the current materials program for NASA, including both in-house and contract research, is approximately sixteen million dollars. It is estimated that fifteen per cent of this effort is on polymeric materials.

In conclusion, let me say, that NASA recognizes the excellent and extensive polymer studies being conducted both in-house and on contract by the Army, the Navy and the Air Force. The cooperation received from the service laboratories in acquainting NASA with their programs and making data available has been, in my experience, most encouraging. I sincerely hope that you will continue to invite us to meetings such as this and that we can establish coordination of our programs to our mutual advantage. In the near future NASA should be in a position to make substantial contributions to your efforts to advance the basic knowledge of polymers.

PROGRAMME STATEMENT ON BEHALF OF U.K. MINISTRY OF AVIATION

W. H. Edwards

Directorate of Materials

Ministry of Aviation

BIRMINGHAM UNIVERSITY

The work of Birmingham University under Professors Stacey and Tatlow in the field of organic fluorine compounds is well known. This group now consists of some twenty workers and over 100 papers on such compounds have been published.

The main Ministry of Aviation interest is in the field of per-fluorinated aromatic and heterocyclic compounds and in polymers and co-polymers based on these. Of the work at present in hand probably the most interesting is that dealing with the hydrolysis of penta-fluoro-phenyl tin chlorides leading to polymers having a tin-oxygen backbone carrying per fluoroalkyl groupsand the study of the decomposition of pentafluorophenyl lithium as a possible route to poly (per fluorophenyl) systems.

Whilst not directly funded from M.O.A. sources, the development, within the University of a pilot scale plant, with supporting workshop, capable of producing quantities up to 5kg of new organic fluorine compounds for further development studies, either as polymers or hydraulic fluids, is of great interest to our work.

DURHAM UNIVERSITY

Under Professor Musgrave, the programme is to develop telomers of narrow molecular weight range by the gamma-irradiation of a mixture of a non-homo-polymerisable olefin with a homo-polymerisable one in the presence of a chain transfer agent.

(Gamma-irradiation has no advantage over more conventional methods of polymerisation initiation, except that cleaner products are obtained. Any interesting material so obtained can then be made in larger quantities by convential methods).

Fluorinated telomers produced by this method are being evaluated as possible plasticisers for fluoro-carbon rubbers. Model compounds based on the Viton structure are being used in another contract (Yarsley Research Laboratories) to study new methods of cross-linking fluoro-carbon rubbers.

NORTHERN POLYTECHNIC

The work on boron chemistry carried out by Dr. Gerrard and his colleagues at Northern Polytechnic is well known. We feel that the main emphasis in this field must be to obtain a better knowledge of the fundamental chemistry involved from which we can then begin to build the type of compound which would appear to give the properties we desire and this is being done at Northern Polytechnic.

At this stage it does appear that non-cyclic polycondensates of dialkylamino-alkyl or aryl borons are of interest as possible linear polymers and these are being studied in greater detail. Factors affecting the formation and hydrolytic stability of substituted borazoles are also being investigated.

MANCHESTER COLLEGE OF SCIENCE TECHNOLOGY

At Manchester the work under Lappert is, at this stage, concerned mainly with the reactions between boron compounds and, in particular, amines. The linking of unsymmetrical aminoborazoles and bisaminoboranes by diamines has been studied and it has been shown that either a cyclic or linear compound may be obtained depending on the relative positions of the two amino groups of the diamine. A number of boron isocyanates have been synthesised and the addition reactions of these with aliphatic and aromatic diamines are being investigated.

YARSLEY RESEARCH LABORATORY

At Yarsley Research Laboratories, work is being concentrated on the development of polymers from difunctional boron-halogen borazole monomers, by reaction with di-Grignard reagents, with organo disodium compounds or by the Wurtz reaction.

Hydrolytic instability is still the main problem with the polymers obtained but it is hoped that by improving the purity of the compounds used, by increasing the molecular weight or by modification of the compound to increase the steric hindrance, this

may be improved.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY

There are three main lines of work at Manchester under Professor Haszeldine. These are:-

(1) Polymers derived from nitroso-compounds
(2) Poly-fluoro-alkyl and poly-cyano-alkyl silicon compounds
(3) Metal co-ordination compounds

The first of these initially started as a study of the addition of fluorinated olefins to nitroso-compounds and this resulted in the nitroso-rubber now being further developed by Minnesota Mining and Manufacturing Company. More recently attention has been paid to the reactions of nitrogen compounds containing a carbon-nitrogen double bond produced by the pyrolysis of oxazetidines.

$$CF_3-N=O + CF_2 = CF_2 \rightarrow CF_3 - \underset{\underset{\displaystyle CF_2-CF_2}{|}}{N} - \underset{\underset{\displaystyle}{|}}{O} \xrightarrow{\text{pyrolysis}} CF_3 - N = CF_2$$
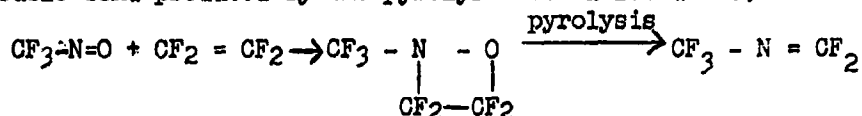
It is well known that in fluoro-alkyl siliconeepolymers, fluid resistance is improved when fluorine is attached to carbon in the alpha position to the silicon. At the same time, thermal stability is satisfactory only when the fluorine is in the gamma position or further from silicon. Study is being made of thermally stable groups which can be attached in the alpha or beta position to silicon and so improve fluid resistance.

Similar studies are in hand with cyano-compounds.

It has been found the perfluoroalkyl groups can be linked to metals, using carbonyl groups as co-ordinating ligands. In such structures, the metal-carbon bond has greater thermal stability. Attempts are being made to prepare polymers of this type, using manganese as the metal.

Complexes of metal carbonyls with olefins containing strongly electro-negative groups are also being investigated. The use of ligands other than carbonyl is being studied.

BIRKBECK COLLEGE, UNIVERSITY OF LONDON

Cage compounds containing silicon and nitrogen or oxygen are being studied by Dr. Shaw at Birkbeck College.

Attempts are being made to prepare derivatives with controlled

functionality for future polymerisation studies.

IMPERIAL CHEMICAL INDUSTRIES

Reasonably thermally stable polymers based on silphenylenes have been developed by I.C.I. but as the polymerisation involves a Wurtz reaction, molecular weights are low. Methods of cross-linking these polymers to improve the physical characteristics are being studied.

OTHER WORK

Other systems which are being examined elsewhere include derivatives of phosphinous acids, compounds of the type $RP(NH_2)_2$. or $RP(NHR')_2$ and polymers produced from these by heating, adducts of silicon hydride-halides with amines, and phosphorus-nitrogen compounds containing fluorinated groups.

DEVELOPMENT WORK

In order to assess the physical properties of experimental polymeric materials produced under our research agreements, methods of tests on the micro-scale are being developed. Thermal stability measurements by thermo-gravimetric analysis are carried out on a routine basis but these are now being extended to measure and identify any decomposition products.

Commercially available rubbers are currently being examined in a number of programmes to determine their properties at high temperatures and after long term high temperature storage. In two programmes, at the Royal Aircraft Establishment and at the Rubber and Plastics Research Association, studies by both continuous and intermittent methods are being made of the stress-relaxation properties of rubber.

Further work has continued on the dynamic properties of rubbers, much of which has been published in the book "Engineering Design with Rubber" by Payne and Scott.

This work is being extended to study the effect of heat treatment on the structure formed by fillers in rubbers, and on the effects of attrited blacks, silicas and silicones on structure.

At the last J.A.N.A.F. Conference an account was given by Mr. Warburton Hall of the Development of Dracones (flexible barges) and collapsible fuel tanks. As a result of this work further attention has been given to the problems of adhesion with particular reference to the adhesion of cured rubber surfaces.

Modifications have been made to the geometry of seams used on Dracones as a result of which a marked improvement in the behavior of these items has been made. Dracones are being used all over the world with much success.

Session II

ELASTOMER PROBLEMS IN
MISSILE SYSTEMS

Chairman: C. B. Griffis
QMR&E Command

SPECIAL POLYMERS FOR ROCKET CASE INSULATION[*]

S. B. Eglin and A. L. Landis
Hughes Aircraft Company
Culver City, California

The requirements for an elastomer to be employed in the formulation of rocket motor case insulation compositions include tensile strength, adhesion and strain tolerance as well as insulative capability. For the motor case application, insulative capability is a function of pyrolytic behavior where the more critical parameters are char-forming properties and the evolution of low molecular weight gases to provide transpirational cooling.

The purpose of this program is to develop a new class of semi-inorganic elastomers which would meet both the mechanical and the insulative requirements of the application. Such a development would represent an advancement of the current state-of-the-art At present, the best available motor case insulation compositions are based on blends of organic rubbers to confer strain tolerance and aromatic resins to confer char-forming properties.

Of the many inorganic and semi-inorganic polymer systems which have been explored in recent years, relatively few have exhibited elastomeric potentialities. Among these are the siloxanes, which have been refined to the stage that they compete with natural and synthetic organic rubbers, and the related random cometalloxanes which contain silicon, oxygen and another element, usually a metal, in the polymer chain and which are in the development stage. From the latter class of copolymers good prospects can be visualized for the development of a semi-inorganic elastomer meeting the mechanical and insulative requirements of the rocket motor case application. First, a random metalloxane copolymer in which siloxy groups are the predominant species in the chain should have elastomeric properties by simple analogy to the

siloxane rubbers. Second, the occurrence of metal atoms in the chain assures retention of mass on pyrolysis and reduces the probability of the formation of high molecular weight volatiles, such as cyclics during pyrolytic decomposition. Development problems can be anticipated relative to the synthesis of random copolymers, the equilibration or rearrangement of these to give the very long chain polymer required for strong elastomers, and the curing of elastomeric gums to yield rubbers. However, the general similarity of the random silicon-containing metalloxane copolymers to the siloxanes indicates high probability that analogous technology could be developed for the random copolymers

The synthesis of homopolymers and alternating copolymers of the metalloxane class which contain one or two metals such as aluminum, arsenic, tin or titanium, have been reported.[1] These polymers are usually, if not always, prepared by a thermal condensation and are mostly oligomers. The copolymers exhibit high second-order transition temperatures, and are low melting resins or glasses, readily soluble in common solvents. The homopolymers are insoluble, infusible substances almost of the nature of the side groups, in marked contrast to the known physical properties of the siloxanes. Even in alternating metalloxane copolymers containing silicon as one of the elements of the chain, the physical properties are more characteristic of soft glasses. However, very low molecular weight fractions of such copolymers may be fluids or waxes having the residual functionality of the monomeric intermediates. Only random copolymers containing silicon as the most frequently occurring metallic element in the chain have exhibited elastomeric properties.[2] [3]

The usual procedure for the synthesis of random copolymers is the cohydrolysis of difunctional organometallic intermediates in the presence of a base as acid acceptor.[4] Another procedure presumed initially to yield ordered copolymers, involves heating of a cyclosiloxane and an organometallic derivative such as a diorganotin oxide.[5] However, the reactants do not polymerize in definite proportions and the products are very high in silicon content probably because of building up of siloxane chains through the catalytic equilibration route.

In this study, a number of random cometalloxanes, including various arsenosiloxanes, aluminosiloxanes, stannosiloxanes and titanosiloxanes have been synthesized. Representative copolymers of these types have been compounded with filters and cured as molded test panels, and evaluated as thermal insulation materials at Rock Island Arsenal.*

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*ASTM Proposed Method of Panel Test for Oxyacetylene Ablation Screening of Thermal Insulation Materials.

In order to facilitate the development of the technology of polymer chain extension, or equilibration, and curing of the random cometalloxane polymers, the Si-O-Sn (stannosiloxane) system was selected as a metalloxane prototype. This selection was based on availability of dialkyltin and diorganosilicon intermediates of high purity and in quantity sufficient to allow extensive polymerization experimentation and, subsequently, detailed studies of equilibration and curing. Functional organometallic intermediates of aluminum, arsenic, and titanium are not available, and it was necessary to synthesize these in the laboratory. It was not convenient to synthesize these in quantities sufficient to allow detailed studies in all areas that are involved in the development of curable elastomers. Further, it is reasonable to assume that technology developed for the Si-O-Sn system would be applicable to Si-O-As, Si-O-Al or Si-O-Ti systems as well, where silicon is the frequently occurring metallic element in the polymer chain.

Using the Si-O-Sn system as a developmental prototype, technology has been developed which has resulted in the bench scale production of stannosiloxane polymer-based rubbers having stress-strain performance comparable to that of commercial silicone rubbers. Stannosiloxane-based compositions have been formulated which showed insulative capabilities, as determined by the proposed ASTM panel test method, substantially superior to those of the best methylphenylsilicone compositions.

The newly developed technology differs materially as to polymerization procedure, chain-extension and curing from that employed in the manufacture of conventional silicone rubbers. The polymerization procedure employed is a high shear interfacial cohydrolysis of difunctional intermediates which results in quanti-tative yields of linear silanol terminated Si-O-Sn polymers having Si:Sn ratios as low as 3:1, depending on the molar ratio of starting materials. Chain extension of the Si-OH terminated polymer was accomplished by treating the polymer, either in bulk or in solution, with a pyridine-diorganodichlorosilane adduct. The curing of the stiff, elastic vinyl-containing Si-O-Sn gums into rubbers was effected by milling in traces of an organic peroxide, or elemental sulfur, followed by the addition of a silicon hydride and heating.

PREPARATION OF RANDOM COMETALLOXANES

Background Considerations

Andrianov, et al.,[6, 7] have employed an interfacial cohydrolysis technique for the preparation of random cometalloxanes such as titanosiloxanes and stannosiloxanes with molecular weights around 100,000, using organic amines or alkalis as acid acceptors. Koenig and Hutchinson,[5] and Okawara and Rochow,[4] by similar procedures prepared random stannosiloxanes having Si:Sn ratios as low as 3:1 . In the former work, a gum was obtained having an

Si:Sn ratio of 20:1 which was reported to have been processed into a rubber, while in the latter work viscous oils were obtained from which a fine white solid, presumably organotin oxide, separated on long standing. Thus, there is evidence that a random Si-O-Sn copolymer can result from the cohydrolysis of difunctional silicon and tin derivatives and some indication that a cometalloxane elastomer could be obtained, although the composition obtained by Koenig and Hutchinson was very low in tin content. It is evident, though, that a substantial improvement in polymerization technique would be required to accomplish the synthesis of long chain random Si-O-Sn copolymers having substantial tin content that are stable to long term hydrolysis or equilibration.

Development of a Polymerization Technique for the Preparation of Random Cometalloxanes

In view of the highly polar nature of the dialkyltin dichlorides, which are actually water-soluble salts, the high shear interfacial polymerization technique, recently employed by Whittbecker and Morgan[8] for the condensation polymerization of polymides, polyphenylesters and the like, appeared to afford a likely route to the preparation of stannosiloxanes.

It can be predicted that the difference in hydrolysis rate between diorganodichlorosilanes and alkyltin dichlorides might be compensated by the affinity of the hydrophilic alkyltin salts for an oil-water interface, considering the vast surface area of an oil-in-water emulsion at high shear. It was, however, recognized that a high concentration of base would be necessary in the aqueous phase since dialkyltin dichlorides hydrolyze only very slowly in water in the absence of base. For the purposes of optimizing hydrolysis conditions to accomplish the synthesis of high molecular weight linear copolymer in a base-catalyzed interfacial cohydrolysis of difunctional silicon and tin intermediates, a Graeco-Latin Square experiment carried out in which dimethyldichlorosilane was employed as the sole hydrolyzable reactant in order that weight average molecular weights could be conveniently determined from bulk viscosities of the siloxane hydrolysis products. This experiment was aimed at definition of optimum conditions including temperature, nature of the solvent, concentration of base catalyst, and detergent in the aqueous phase, concentration of reactants in the organic phase, and volume ratio of aqueous and organic phases. The base employed was potassium hydroxide. Preliminary experiments showed that a base having high equivalent weight yielded siloxanes of highest bulk viscosity in interfacial cohydrolysis experiments. A relatively high solute content in the aqueous phase is consistent with "scarce water" hydrolysis conditions , and hence should favor formation of linear polymers.

A total of 18 small-scale hydrolysis runs was carried out in this experiment using 0.15 mole of dimethyldichlorosilane in a

small laboratory blender with a one-quart capacity stainless steel blender jar equipped with a steel jacket for cooling. In the recovery of the siloxane hydrolysis products from the organic layer in these runs, the solvent was removed under vacuum without application of heat to avoid thermal condensation of the silanol-terminated siloxane chains, which would have vitiated the results of the experiment. From measurements of bulk viscosities of the siloxane fluids obtained as hydrolysis products in these small scale runs measured in a small specially constructed viscosity pipette, a clear trend was evident in the measured viscosities which ranged from 13 to 2925 centistokes. The maximum viscosity observed corresponds to an $\overline{M}_W$ value of 55,000 for linear polydimethylsiloxane. The optimum reaction conditions indicated for the preparation of linear siloxanes by the results of this experiment were presumed to represent the most logical hydrolysis conditions for initial cohydrolysis experiments aimed at the synthesis of linear stannoslioxane polymers, particularly where a high molar ratio of silicon to tin intermediates was sought. It was not possible, through analysis of the viscosity data, to determine which variables were critical. However, the formulation which yielded polydimethylsiloxane fluid of the highest bulk viscosity (2925 cs) was:

<u>Organic Phase:</u> Me_2SiCl_2 0.15 m in 125 ml. CH_2Cl_2 at 25°C.

<u>Aqueous Phase:</u>   KOH 0.375 m. and Alconox 0.6 g in 125 ml H_2O at 0°C.

<u>Dispersion:</u>   Two minutes at high speed in ice-water cooled blender.

<u>Recovery:</u>   Phases separated by centrifugation, solvent removed under vacuum without heat.

It was subsequently found that larger batches (0.2 - 0.25 moles of intermediates) could be run in the small blender by increasing the volumes of the aqueous and organic phases, holding concentration constant. Increasing the batch size did not affect molecular weight, provided that the initial temperatures of the two phases were reduced sufficiently to control the maximum emulsion temperature within a range of 25 ±2°C.

Preparation of Random Stannosiloxane Polymers

Subsequently, the interfacial, by analysis technique described above, was employed in small scale (0.2 - 0.25 moles of intermediate) runs for the preparation of linear Si-O-Sn polymers at Si:Sn ratios varying from 3:1 to 6:1. Clear, stiff gums were obtained in each of these initial runs. $\overline{M}_N$ values determined cryoscopically in benzene, varied from 3-10,000. These products were obtained in essentially quantitative yields based on starting intermediates. It was observed that residual solvent was difficult

to remove below a level of 2-3%. Several days pumping under ·
vacuum was necessary in order to reach constant weight. The gums
exhibited dilatent properties, the stiff gums breaking sharply under
sudden stress, and exhibiting very slow cold flow. Bulk viscosities
appeared to be orders of magnitude greater than those of poly-
dimethylsiloxanes of comparable molecular weights.

The preparation of stannosiloxane polymers having Si:Sn
ratios as low as 3:2 was attempted. However, these compositions,
which actually contained three times as much tin as silicon by
weight in the chain,were oligomers and either contained white pre-
cipitates of organotin oxides as prepared, or such precipitates
formed in the gums within a few days of preparation. In general,
stannosiloxanes prepared at Si:Sn ratios less than 4:1 slowly
developed a turbidity unless stored in a dessicator or in a refriger-
ator at 0°C or less.

The use of a mixture of trifunctional and difunctional
chlorosilanes with dialkyltin dichlorides, however, yielded Si-O-Sn
gums at Si:Sn ratios as low as 3:2. These copolymers were initially
clear, and did not develop turbidity even when exposed in the atmos-
pheres for indefinite periods. These polymers, however, were
definitely resinous in character although they did not harden on long
standing as would have been expected had the polymer chain con-
tained functional side groups   Formulations employed in the pro-
portion of representative polymers, are given in Table I, infrared
spectra are shown in Table II.

Stannosiloxane Polymers from Di- and Trifunctional
Silicon and Difunctional Tin Intermediates

Cohydrolysis of Dimethyldichlorosilane, Phenyltri-
chlorosilane and Dibutyltin Dichloride

B-3971-21 - Dimethyldichlorosilane (15.5 g., 0.12 mole) and
phenyltrichlorosilane (12.7 g., 0.06 m.) were dissolved in
125 ml. of ethanol-free chloroform and dibutyl tin dichloride
(21.3 g., 0.07 mole) was added and dissolved. Then a solution
of potassium hydroxide (28.5 g., 0.5 m.) potassium carbonate
(13.8 g., 0.1 m.), and Alconox detergent (1 g.) in 125 ml. of
distilled water was cooled to -10°C and placed in an ice-
water jacketed laboratory blender. The chloroform solution,
also cooled to -10°C, was rapidly added with stirring at
moderate speed. The resulting emulsion was stirred at high
speed for four minutes. The emulsion was centrifuged to
separate the aqueous and organic phases and the solvent re-
moved from the chloroform layer under reduced pressure.
The product, a colorless, rubbery solid (25.6 gr., Theory
33.9 g.) had a molecular weight of 1800 (cryoscopic), was
soluble in common solvents, and melted between 145-150°C

No.	Intermediates	Moles	Initial Temp °C Aqueous	Organic	Detergent	$\overline{M}_n$ Cryoscopic	Product
B-3971-21	MeSiCl$_2$	0.12	-10,	-10	1 g.	1800	Soluble, fusible rubbery solid
	ϕSiCl$_3$	0.06					
	Bu$_2$SnCl$_2$	0.07					
B-3971-23	Me$_2$SiCl$_2$	0.15	-10,	-20	1 g.	2150	Soluble, fusible rubbery solid
	MeViSiCl$_2$	0.07	-10,	-20			
	ϕSiCl$_3$	0.02					
	Bu$_2$SnCl$_2$	0.07					
B-3971-25	Me$_2$SiCl$_2$	0.09	-10,	-25°C	None	1400	Stiff elastomeric gum
	MeCiSiCl$_2$	0.01					
	MeViCl$_3$	0.05					
	BuSnCl$_2$	0.10					
B-3971-26	Me$_2$SiCl$_2$	0.13		-40°	None	1300	Stiff elastomeric gum
	MeViSiCl$_2$	0.01					
	MeSiCl$_3$	0.03					
	Bu$_2$SnCl$_2$	0.08					

Organic solvent: Ethanol-free chloroform
Acid Acceptor: KOH 0.4, K$_2$CO$_3$ 0.25 equivalents.
Detergent: Alconox

Table I. Stannosiloxane polymers from cohydrolysis of di- and trifunctional silanes and dibutyltin dichloride.

B-3971-21	B-3971-23	B-3971-25	B-3971-26	INTERPRETATION
3010 sh	3010 sh			C-H stretch
2930 s	2900 s	2920 s	2490 s	C-H stretch
		2900 s		C-H stretch
2840 sh	2840 sh	2840 sh	2840 sh	C-H stretch
1590 w	1590 m	1600 broad	1610	poss. vinyl C=C
		1560 m	1570 m	C-C skeletal
1460 m	1455 s	1455 m	1455 m	C-CH def.
1425 m	1420 sh			Si-$\emptyset$
1410 sh	1405 m	1405 vw	1405 w	Si-CH$_3$
1375 s	1370 s	1370 m	1375 m	C-CH$_3$ def.
1335 sh	1340 sh		1315 w	C-H def.
1255 s	1255 s	1255 s	1255 s	Si-CH$_3$
1120 sh				Si$\emptyset$
1075 broad	1060 broad	1070 broad	1075 broad	Si-O-Si
1030 s	1020 sh	1030 sh	1035 s	
940 sh	925 sh	930 broad	945 sh	Si-O-Sn
	860 sh	865 sh	920 w	
835 m	830 sh	835 sh	845 broad	
795 s	785 m	797 s	795 s	Si-CH$_3$
730 sh	737 w	740 sh	740 sh	
697 m	685 s	665 m	ca 670 s	Si-O-Sn

s – strong   m – medium   w – weak   sh – shoulder

Table II.   Infrared spectra of stannosiloxanes containing trifunctional siloxane linkages in Cm^{-1} .

Anal. Found: % carbon 38.95, Hydrogen 6.48

Calc. % carbon 41.1, Hydrogen 6.71

B-3971-23 - Dimethyldichlorosilane (19.4 g., 0.15 mole) phenyltrichlorosilane (4.2 g., 0.02 mole), methylvinyl-dichlorosilane (1.4 g., 0.01 mole) were dissolved in 150 ml. of alcohol-free chloroform and dibutyltin dichloride (21.3, 0.07 mole) was added and dissolved. A solution of potassium hydroxide (22.8 g., 0.4 mole) potassium carbonate (17.5 g., 0.125 mole) and Alconox (1 g.) was cooled to -10°C and placed in the ice-jacketed blender. The chloroform solution, cooled to -20°C, was then rapidly added with stirring at moderate speed. The resulting emulsion was then stirred at high speed for four minutes and the organic phase separated by centrifugation. On removal of chloroform under reduced pressure, a white rubbery solid (25.3 gm., 31.9 gm. theory) was recovered, which was soluble in common solvents, melted from 140-145°C, and had a molecular weight (cryoscopic in benzene) of 2200.

Anal. Found: % carbon 37.62, % Hydrogen 7.21

Calc. % carbon 37.93, %Hydrogen 7.16

Cohydrolysis of Dimethyldichlorosilane, Methyl-trichlorosilane and Dibutyltin Dichloride (Tables III, IV)

B-3971-25 - Dimethyldichlorosilane (11.6 g., 0.09 mole) methylvinyldichlorosilane (1.4 g., 0.01 mole) and methyl-trichlorosilane (7.5 gm., 0.05 mole) were dissolved in 135 ml. of ethanol-free chloroform and dibutyltin dichloride (30.4 g., 0.10 mole) was added and dissolved. A solution of potassium hydroxide (22.4 g., 0.4 mole) and potassium carbonate (17.5 g., 0.125 mole) in 135 ml. of distilled water was cooled to -10°C and placed in an ice-water jacketed laboratory blender. The chloroform solution, cooled to -25°C was then rapidly added with stirring at moderate speed. Stirring was continued at high speed for four minutes. The organic layer was separated by centrifugation and the chloroform solvent was removed under vacuum. The product, a clear elastomeric gum (32.2 g., 35-65 g. theory), had a molecular weight of 1400, determined cryoscopically in benzene.

Anal. Found: % Carbon 35.17, % Hydrogen 6.91

Calc. % Carbon 35.73, % Hydrogen 7.16

B-3791-26 - Dimethyldichlorosilane (16.9 g., 0.13 mole), methylvinyldichlorosilane (1.4 g., 0.01 mole) and methyl-trichlorosilane (4.5 g., 0.03 mole) were dissolved in 135 ml. of ethanol-free chloroform and dibutyltin dichloride

(24.3 g., 0.08 mole) added and dissolved. A solution of potassium hydroxide (22.8 g., 0.4 mole) and potassium carbonate (17.5 g., 0.125 mole) was cooled to -5°C and placed in an ice-water jacketed laboratory blender. The chloroform solution, cooled to -40°C, was then rapidly added with stirring at moderate speed. After four minutes stirring at high speed, the resulting mixture was centrifuged and the organic layer recovered. Upon removal of solvent under reduced pressure, a clear elastomeric gum (30 g., 32.3 theory) remained. The product had a molecular weight of 1300, determined cryoscopically in benzene.

Anal. Found: % Carbon 35.45, % Hydrogen 7.16

Calc. % Carbon 35.79, % Hydrogen 7.33

Andrianov[1] prepared stannosiloxanes in a similar manner and ascribed a ladder-like structure to the polymer chain, and it might be inferred that trifunctional silanes were employed here also to confer stability toward hydrolysis or equilibration to the Si-O-Sn polymers.

Qualitative differences were observed among the various diorganotin dichlorides as to reactivity in hydrolytic condensations with difunctional silanes Based on maximum proportions of organotin intermediates which can be incorporated into Si-O-Sn polymers, the order of decreasing reactivity of diorganotin dichloride is dimethyl > dibutyl >> diphenyl. This observation is consistent with the predicted hydrophilic nature of these intermediates based on the nucleophilic character of the organic substituents.

The occurrence of white precipitates in stannosiloxane polymers, particularly after long standing, has suggested to Okawara and Rochow[4] that the products obtained on cohydrolysis of diorganotin and diorganosilicon intermediates might not be actual polymers, but that separation of diorganotin oxide might result from slow condensation of Sn-OH groups within a solvent medium of silicone polymer. Molecular rearrangement was also suggested by these authors as a possible cause of the separation of organotin oxide.

In order to resolve the question as to the physical state of these cohydrolysis products, fractionation was undertaken on a polymer prepared at 2:1 Si:Sn ratio from diacetoxytin and diacetoxysilicon intermediates to facilitate the identification of terminal groups by infrared spectra with subsequent characterization of the fractions as to molecular weight and infrared spectra. The procedure employed in fractionation consisted of sequential of freezing of a polymer solution in methylene chloride and thawing under centrifugation, decanting of the liquid and recovery of a supernatant layer of stiff transparent gum. This procedure was repeated until four portions had been recovered, then the solvent was removed

from the remainder under vacuum, and the fifth fraction, a thin yellow oil, was recovered. Molecular weight determinations carried out on the benzene soluble fraction by the cryoscopic method are given in Table III.

Fraction	Weight, Gms	Cryoscopic Molecular Weight
Zero Fraction	1.6	(Insoluble)
Fraction I	12.5	2200
Fraction II	4.7	1800
Fraction III	3.3	(Insoluble)
Fraction IV	5.1 (liquid)	400

Table III. Fractionation of stannosiloxane polymer.

The total weight of all fractions was 27.2 g., about 70%, not accounting for losses.

A small amount of white, wax benzene insoluble material, designated as zero fraction, was recovered from the walls of the centrifuge bottles. One subsequent fraction (III) became insoluble on exposure to the atmosphere possibly because of hydrolysis acetoxy end groups.

Infrared spectra data for the fractions (I-IV) are given in Table IV. Absorption bands believed to be assignable to vibrations of Si-O-Sn linkages were observed in all fractions. An absorption characteristic of the carbonyl vibration, indicating presence of terminal acetoxy groups, was found in the liquid fraction (IV) but in no other fraction.

Considering that cryoscopic data indicated efficient fractionation on the basis of polymer chain length, the similarity of composition of the several fractions shown by the IR spectra comprise good evidence that these products are actually Si-O-Sn polymers.

The necessity for the preparation of substituted quantities of Si-O-Sn polymers .ur process development studies of polymer chain extension, or catalytic equilibration, and curing, required scaled-up preparation of these copolymers. This was accomplished with no particular difficulty through the use of a large laboratory blender with a jacketed stainless steel blender jar of one-gallon capacity and five-fold increase in quantity of reactants, (from 0.2 to 1.2 mole) and solvents.

FRACTION I	FRACTION II	FRACTION III*	FRACTION IV	ASSIGNMENT
3330 vw	3330 vw	3330 vw	3330 vw	OH stretch
2930 s	2930 s	2940 s	2900 sh	CH stretch
2850 m	2840 m	2850 m	2850 broad	CH stretch
1735 vw			1725 s	
1615 m	1610 m	1610 w	1630 s	C = O
1575 m	1575 m		1575 s	
1460 m	1460 m	1460 w	1445 sh	C-CH$_3$ def.
1410 m	1415 m		1410 s	Si-CH$_3$
1375 s	1375 s	1375 s	1370 s	C-CH$_3$ def.
1305 m	1305 m	1300 sh	1290 sh	
1255	1255 s	1255 s	1255 s	Si-CH$_3$
1155 sh	1155 sh	1155 w	1155 sh	
1080 broad	1080 broad	1080 broad	1090 s	Si-O-Si
1020 broad	1025 broad	1015	1015	Si-O-Si
925 m	925 m	930 m	920 w	
865 sh	865 sh	860 broad	860 broad	Si-O-Sn
855 m	855 m			
790 s	795 s	790 s	800 s	CH$_3$ def.
675 m	675 m	675 m	680 broad	Si-O-Sn

*III KBr disc.

m – medium, w – weak, sh – shoulder

Table IV. Infrared spectra of stannosiloxane polymer fractions in Cm^{-1}.

Some modifications of composition of cohydrolysis mixtures were made in the preparation of most large-scale (1.0 mole of intermediates) batches of Si-O-Sn polymers, consisting of the addition of small percentages of vinylalkyldichlorosilanes, vinylaryldichlorosilanes, or methyldichlorosilanes to incorporate crosslinking functionality into the products.

CATALYTIC REARRANGEMENT AND CHAIN EXTENDING REACTIONS OF STANNOSILOXANE POLYMERS

The first experimental approach employed in attempting to increase polymer chain length was to reproduce the conventional catalytic equilibration procedures employed with cyclic and linear siloxanes. In the absence of clear-cut evidence for the occurrence of substantial fraction of cyclic stannosiloxanes in the cohydrolysis products, it was assumed that the products consisted of essentially silanol-terminated polymer chains, even though only weak OH absorption was observed in infrared spectra (Table IV). Rearrangement to yield long chain polymers could occur if water of condensation could be eliminated whether or not an equilibration catalyst were employed. In view of the observed behavior of some polymers to actually gain weight over a period of days in a saturated atmosphere of water vapor, in addition to the extremely high bulk viscosity of even low molecular weight polymers, it was recognized that the elimination of water of condensation might not be possible under a stream of nitrogen, or even under vacuum. It was found, in fact, in repeated experiments, that water of condensation could not be expelled for bulk polymer on heating with or without nitrogen flushing or under vacuum, whether or not catalysts were employed.

When strongly acidic or basic equilibrium catalysts, such as sodium hydroxide, alkali silanolates, sulfuric acid, benzene sulfonic acid and the like, were employed at low concentration (0.1%) no change in bulk viscosities occurred after heating at 100-130°C for periods of several hours. At higher catalyst concentrations, or at higher temperatures (130-150°C), turbidity developed indicating separation of organotin oxides.

Transient catalysts, such as quaternary ammonium hydroxides and phosphonium hydroxides, actually lead to lowering of bulk viscosity, presumably because it was necessary to use these as aqueous solutions, or hydrates, and the added water equilibrated with polymer resulting in shorter chain lengths by providing additional chain-terminating hydroxy groups. Friedel-Crafts catalysts such as boron trifluoride and aluminum trichloride initially resulted in sharp increase in bulk viscosities when employed with solutions of polymer in organic solvents, however, the viscosity rapidly decreased with time because of degradation by mineral acids formed on the hydrolysis of catalyst. Some separation of organotin oxide also occurred in these cases.

Therefore, because of the failure to remove water of condensation from bulk polymer by physical means, it was apparent that a means of chemical scavenging of water would be required if thermodynamic equilibration of stannosiloxane were to be shifted in the direction of chain extension rather than depolymerization.

The separation of organotin oxide, or of stannoxy-terminated oligomer, in these equilibration experiments is a clear demonstration of the non-equivalence of the stannoxy and siloxy terminated polymer fragments with respect to the facility of addition of another chain fragment by the catalytic equilibration route.

Okawara and Rochow[4], who reported that organotin oxide separated from fluid stannosiloxane polymers, suggest that a process of rearrangement was one of the possible explanations. In the current study, the separation of organotin oxides from low viscosity Si-O-Sn polymers on long standing was also observed, as discussed in the previous section. No such occurrence has been noted in very high viscosity Si-O-Sn polymers prepared from difunctional intermediates or in any polymers prepared from mixtures of di- and trifunctional intermediates. These essentially solid polymers would be characterized by highly restricted segmental mobility and diffusion rates of water and other reactive species in this mixture would be very low.

The importance of the relative reactivity of siloxy and stannoxy-terminated polymer fragments toward addition of another fragment by the equilibration route is quite apparent. If the siloxy-terminated fragments are more reactive than the stannoxy-terminated fragments, then prospect for obtaining long chain polymers by equilibration involving elimination of water of condensation from silanol terminated linear Si-O-Sn polymer is remote.

Because of these considerations, a means was sought for chemically scavenging water produced on the condensation of SiOH or SnOH, if such exist. A number of water scavengers were investigated with both bulk polymer and polymer in solution in hydrocarbon solvents. Reagents investigated included diisocyanates, metal alkoxides and acid anhydrides. These all appeared to increase viscosity through chain extension by reaction with the silanol terminated groups, but did not yield compositions exhibiting attractive elastic properties. It was then sought to accomplish the same objective with a diorganodichlorosilane employing an adduct of pyridine and diorganodichlorosilane. In this case, the hydrogen chloride produced by the reaction of diorganodichlorosilane and -OH terminated group, would be neutralized by the pyridine and hence be removed from the system, and thereby preventing degradation of polymer. This procedure proved to be quite effective, apparently accomplishing direct chain extension when employed with polymers in bulk, or in the presence of minimal quantities of solvent. When the pyridine-diorganodichlorosilane adduct was added to dilute

solutions (25% solids) of polymer in benzene at room temperature, addition of an -R$_2$SiCl group to each terminal SiOH apparently occurred, with no change in solution viscosity. Upon removal of solvent and subsequent exposure to a stream of air at room temperature, hydrolytic condensation of the Si-Cl terminated polymer occurred yielding a strong, tough, elastic gum without indication of separation of organotin oxides.

Chain Extension Reaction of Stannosiloxane Polymer in Bulk

To approximately 50 grams of polymer B-4337-60 were added 10 ml of methylphenyldichlorosilane. Then 10 ml of pyridine was added in an exothermic reaction. The resulting pyridine dihydrochloride was separated by the addition of 100 ml of hexane and centrifuging the resulting viscous solution. The polymer solution was concentrated by removal of hexane under vacuum, and a sharp increase in viscosity was observed. The recovered polymer was gummy and elastic, but was sufficiently fluid to be transferred to a large Petri dish. After a short exposure to the atmosphere the polymer solidified to a tough elastic gum. The polymer was benzene soluble but exhibited no measurable effect on the freezing point of the solvent.

Chain Extension Reaction of Stannosiloxane Polymer in Benzene Solution

To 50 gms of polymer B 5201-33 were added a solution of 30 ml of dimethyldichlorosilane and 30 ml of pyridine in 100 ml of benzene. An exothermic reaction took place. The volatile components of the reaction mixture were removed by vacuum distillation without the use of any external heating. Then 100 ml of hexane was added. The pyridine dihydrochloride was removed by centrifugation. The excess hexane was removed under vacuum. Then the residue, which was a relatively clear liquid, somewhat lower in bulk viscosity than the starting polymer, was exposed in a shallow dish to the atmosphere. During the course of a day, the bulk viscosity of the polymer increased until it had reached that of a tough elastomeric gum. The resulting gum was slowly soluble in benzene but exhibited no measurable effect on the freezing point of the solvent.

CURING OF STANNOSILOXANE POLYMERS

Stannosiloxane polymers which contain functional side groups, that is, vinyl or -SiOH, and which have high molecular weights, can be readily cured to strong rubbers using organic peroxides or silicon hydrides with an appropriate activator. The

latter applies only to stannosiloxane polymers which have been chain-extended by the dichlorosilane/pyridine procedure described in the previous section, and are, at the time of addition of curing agents, actually elastomeric gums exhibiting no dilatant character. It is not known as yet whether a stannosiloxane polymer not containing vinyl side groups can be cured with organic peroxides, or whether a vinyl-containing stannosiloxane polymer can be cured with free radical catalysts other than peroxide.

Stannosiloxane polymers, as they are obtained as initial cohydrolysis products exhibiting dilatant properties, have not been cured with peroxides. They are readily cured with silicon hydrides and appropriate activators, but the cured compositions are weak and brittle and break under load without elongation. Low molecular weight stannosiloxanes yield stiff brittle solids when exposed to large doses of ionizing radiation up to 94 megarads from a Cobalt 60 source. Under smaller doses depolymerization was the only discernible effect although cross-linking by the free-radical mechanism undoubtedly occurred.

The ability of the silicon hydrides, disilylbenzene and the polymeric silane $(MeHSiO)_n$, to cure low molecular weight stannosiloxanes, while the peroxides do not, is probably due to the fact that the silicon hydrides, which react by addition in the case of vinyl groups or by condensation in the case of -SiOH groups, form an actual part of the cross-link and do not require that the reactive sites on neighboring chains be in such close proximity as is necessary for cross-linking by the free radical mechanism.

Effective use of the silicon hydrides as curing agents for low molecular weight stannosiloxane polymers containing vinyl functionability, requires the use of an activator, although partial cures can be effected with the silicon hydrides alone. For polymers containing -OH side groups, complete cures occasionally result without the use of an activator, depending on frequency of functional side groups on the chain and on polymer chain length. The substances so far found to be effective as activators for silicon hydrides are organic peroxides, elemental sulfur and metal chelates. All of these substances react with hydrides.

EVALUATION OF STANNOSILOXANE-BASED COMPOSITIONS AS THERMAL INSULATION MATERIALS

Preliminary evaluation of a number of cured stannosil-oxane-based compositions has been carried out at Rock Island Arsenal by the ASTM Proposed Method of Panel Test for Oxyacetylene Ablation Screening of Thermal Insulation Materials. These compositions were for the most part asbestos-filled stannosiloxanes, cured with disilylbenzene using either a metal chelate activator, or

44

no activator. None of the compositions so far evaluated by ablation screening were prepared from Si-O-Sn polymers which had been chain-extended by the diorganodichlorosilane-pyridine procedure described previously. The polymers used in the formulation of these compositions were (dialkyl) stanno (dimethylvinyl) siloxanes and (dialkyl) stanno (methylphenylvinyl) siloxanes having number average molecular weights of 2000-2500. The cured asbestos or silica-filled compositions exhibited elasticity and recovery from deformation, however, they were quite low in tensile strength, breaking under load without measurable elongation. These deficiencies in stress-strain performances have been substantially eliminated in compositions prepared according to the technology later developed for chain-extending and curing of random cometalloxanes.

Results of ablation screening tests shown in Table V indicate significant promise for stannosiloxane-based compositions as thermal insulation materials Based on torch indices, P_{200}, the (dialkyl) stanno (dimethylvinyl) siloxane-based compositions, performed significantly better than comparable methylphenylvinylsilicone-based compositions. This indicates that the stannosiloxanes have char-forming properties superior to those of the siloxanes, probably in consequence of postulated difference in the mode of thermal decomposition between stannosiloxanes and siloxanes.

Stannosiloxanes containing a substantial proportion of phenyl substituent in the side chains, the (dialkyl) stanno (methylphenylvinyl) siloxanes (Table VI), did not perform as well in the ablation screening test as did stannosiloxanes containing no phenyl substituent. This result was in direct contrast to what had been expected, since the substitution of phenyl groups for alkyl side chains has been postulated to improve char-forming properties. It is believed that the failure of phenyl-containing stannosiloxanes to perform as anticipated in the ablation screening test was due to incomplete curing. These compositions were compounded and cured using silicon hydrides without the use of the necessary activator, it not having been recognized at the time that silicon hydrides alone do not effectively cure stannosiloxanes.

The earlier compositions compounded from (dialkyl) stanno (dimethylvinyl) siloxanes were also formulated and cured before it was known that an activator was required with the silicon hydrides. However, in these instances a low percentage of a metal chelate derivative had been incorporated into the polymers in an effort to produce a copolymer which would spontaneously cure upon heating. The self-curing effect was not achieved, however, a number of batches of stannosiloxane polymer were prepared which did contain small proportions of chelate groups in the polymer chain. For this fortuitous reason, a number of these earlier compositions were found to be quite readily cured with silicon hydrides.

45

Sample Number	Composition	Density	Insulation Index P_{200}*	Erosion Rate
B-4346-38	(dibutyl) stanno (dimethylvinyl) siloxane silica (Cab-o-Sil)	1.10	46.8	6.2
B-4346-39	(dimethyl) stanno (dimethylvinyl) siloxane asbestos	—	34.8	6.2
B-4346-40	(dimethyl, dibutyl) stanno (dimethyl, methyl-phenylvinyl) siloxane., asbestos	—	44.8	5.0
B-4346-34	(dibutyl) stanno (dimethylvinyl) siloxane phenolic resin (Durez 12687), silica	1.13	52.0	4.9
RIA-Z56C5F2	(methylphenylvinyl) siloxane, asbestos	1.30	27.0	9.8
RIA-N-141F	Nitrile rubber - phenolic resin, asbestos	1.43	77	2.6

*ASTM Proposed Method of Panel Test for Oxyacetylene Ablation Screening of Thermal Insulation Materials.

Densities are approximated.

Table V. Ablation screening evaluation of dialkylstannosiloxane-based compositions - Rock Island Arsenal.

Sample Number	Composition	Density	Insulation Index P200*	Erosion Rate
B-4870-3	(dimethyl) stanno (dimethyl, methyl) siloxane, asbestos	1.11	38.6	8.4
B-4870-8	(dibutyl) stanno (methylphenylvinyl) siloxane, asbestos	1.67	32.5	6.3
B-4870-15	(dibutyl) stanno (methylphenylvinyl) siloxane, asbestos	1.55	33.4	7.1
B-4870-16	(dibutyl) stanno (methylphenylmethyl) silicone, asbestos	1.57	33.1	5.4
RIA-Z556C5F2	(methylphenylvinyl) siloxane, asbestos	1.30	27	9.8
RIA-N141F	Nitrile rubber, phenolic resin, asbestos	1.43	77	2.6

*ASTM Proposed Method of Panel Test for Oxyacetylene Ablation Screening of Thermal Insulation Materials.

Densities are approximated.

Table VI.   Ablation screening evaluations of alkylphenylstannosiloxane-based compositions — Rock Island Arsenal.

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FLEXIBLE, THERMAL INSULATION FOR SOLID PROPELLANT ROCKET MOTORS

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During the last few years emphasis has been placed on the development of flexible materials to insulate the structure of a solid propellant rocket motor from the hot propellant gases. Flexibility is a desirable property because the motor case strains elastically under the internal pressure generated during firing. If the insulation does not expand with the motor, it can facture, allowing the hot gases to penetrate to the case wall. If the insulation is bonded to the grain and to the motor case, flexibility is essential to prevent fracture of the bond and motor failure by side burning.

Although a superior insulation must meet many requirements, we have generally limited ourselves to what we consider the three prime properties, (1) flexibility of the filled and unfilled resin, (2) the insulation performance of the filled resin, and (3) the density of the filled resin.

For a steel case, the maximum elastic strain is approximately 0.8 per cent. Incorporation of a ten-fold safety factor gives a desired minimum deformation of 8 per cent for the insulation. Since the motor reaches full pressure in approximately 0.1 sec, measurements are made at strain rates of 4.8 in/in/min or greater.

Although the insulation performance of a material may be determined by several laboratory methods, eventual evaluation in an actual motor firing is, of course, necessary. We generally test our materials in 5-inch motors containing aluminized propellants with theoretical flame temperatures of 5600°F or 6500°F and operating pressures of up to 1000 psi, for durations usually of 30 to 60 seconds. Char rate is the insulation parameter generally reported; the lower the char rate the better the performance.

Since weight reduction is important in rocket design, an insulation of otherwise good performance may be eliminated because of its high density. Thus, improvement in density as well as char

rate is sought for the various resin-filler systems.

In Figure 1 are shown the various areas of thermal insulation in a rocket motor. We are primarily concerned with the case-wall and the nozzle-approach insulation. The service conditions are more severe in the nozzle-approach section than along the motor wall because of the higher gas velocity, greater gas turbulence, and greater particle impingement. In Figure 2 are shown specimens in a peripheral slab section (case-wall environment) for evaluation in a static motor firing. The hot propellant gases flow through the ring and thus parallel to the exposed face of each specimen. In Figure 3 are shown specimens mounted for evaluation in a convergent section (nozzle-approach environment).

This paper describes some of our work on the development of flexible polymers for rocket motor case insulation under the Department of Army Contract Number DA-36-034-ORD-3325-RD. Resin systems selected for study were the epoxies, phenolics, melamines, urethanes, furans, and the polyesters. When possible we have tried to work with readily available commercial materials.

Several types of epoxy resins have been investigated. These include the bis-phenol A-epichlorohydrin system, epoxidized polyolefins, and novolac epoxy resins. Both internal and external plasticizers were investigated. A practical external plasticizer could not be found. However, numerous internal plasticizers, such as liquid polysulfide resins, polyamides, polyesters, certain specially prepared anhydrides, dimer acids, and castor oil, successfully introduced flexibility into one or more of these various epoxy resins.

Commercial and specially prepared A-stage, phenol-formaldehyde resins were successfully flexibilized with certain epoxy and polysulfide resins.

Attempts to prepare flexible melamine resins by reacting melamine or methylol melamine with diisocyanates, polysulfides, epichlorohydrin, polyamide resins, polyols, and certain epoxy resins were unsuccessful. However diallyl melamine could be cured to a flexible material with several epoxy resins.

Flexible urethane resins were prepared by reacting poly-isocyanates with long-chain polyols such as castor oil.

Initial studies with furfuryl alcohol indicated that a flexible furan resin could be prepared by use of specially prepared acid catalysts.

Studies on polyester resins only recently began.

Time permits only a discussion of two of our more promising flexible resins: a castor oil-modified, epoxy-anhydride resin and an
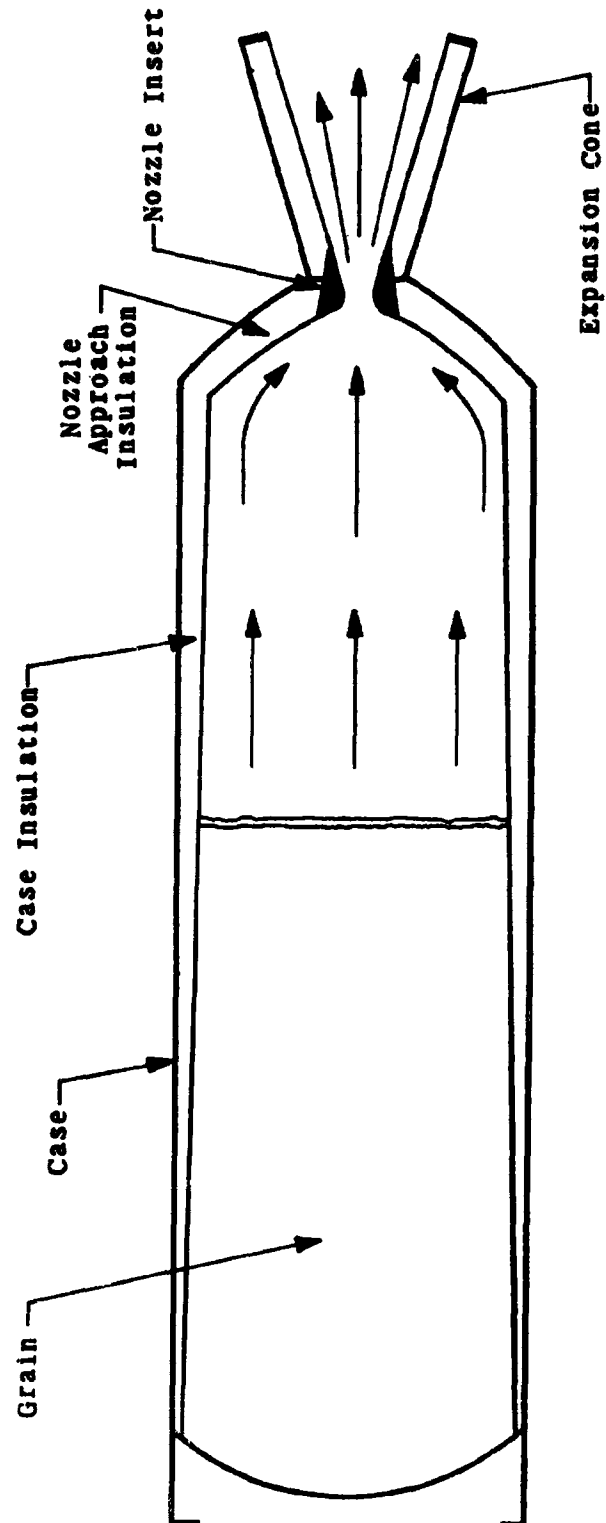
Figure 1. Cross Section of End-Burning Solid-Propellant Rocket Motor.
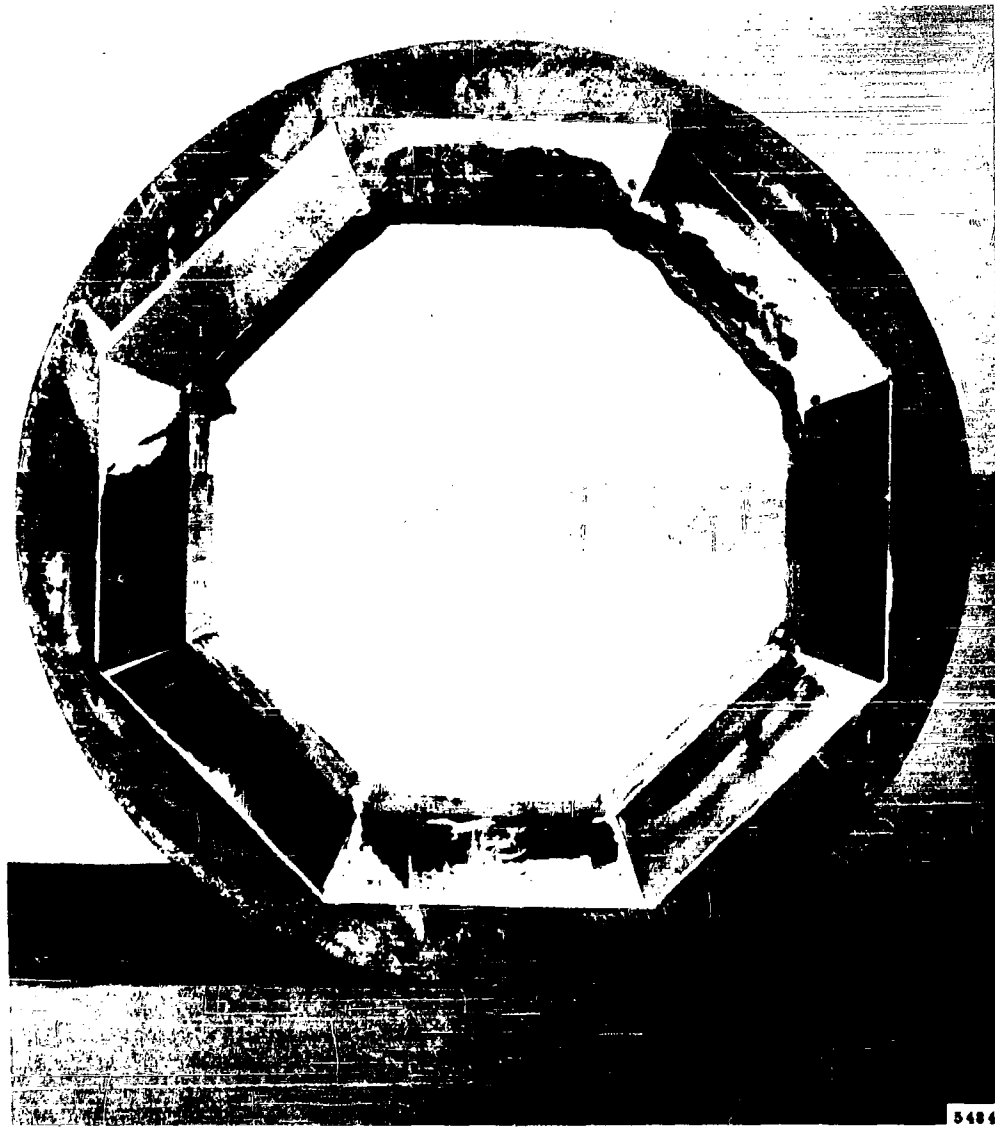
Figure 2. Test Specimen in the Peripheral-Slab
Section Before Motor Firing.

Figure 3. Test Specimens in the Convergent
Section Before Motor Firing.

epoxy-modified, phenol-formaldehyde resin.

Figure 4 shows the ingredients used to prepare a flexible epoxy resin which, when filled with 40 per cent of asbestos fiber, is an excellent insulator. A formulation of only the epoxy resin and the anhydride (10:9 ratio) results in a good, but rigid insulation. By adding castor oil, longer chain lengths are introduced between the points of cross linking with a resultant increase in flexibility. When castor oil is added, however, a proportional amount of anhydride is also added to react with the hydroxyl groups of the castor oil. The stoichiometric amount of castor oil and anhydride to yield the desired percentage of castor oil is determined by the simultaneous solution of two equations.

In Table I are shown the elongation and tensile strength of unfilled formulations containing various amounts of castor oil. Further evaluation showed that a resin containing 40 per cent of castor oil could be prepared with good properties whereas a concentration of 50 per cent did not completely cure. Obviously, asbestos as a filler would reduce the flexibility of the insulator. As an example, a 30-per cent-castor oil modification filled with 40 per cent of asbestos fiber had 19 per cent elongation and 1210 psi tensile strength (20 in/in/min strain rate; 1-inch gage length).

TABLE I

Effect of Castor Oil on the Mechanical Properties of
Unfilled, Epoxy-Anhydride Resins Modified with Castor Oil

Castor Oil Content (per cent)	Ultimate Elongation [a] (per cent)	Ultimate Tensile Strength [a] (psi)
0	1	2710
10	5	4610
30	42	3280
35	150	1400

a. Strain rate was 5 in/in/min. Gage length was 4 inches.

In addition to the increase in flexibility, the insulation performance also improves (lower char rates) as the concentration of castor oil is increased. Table II shows the motor-test results for 0-, 10-, 20-, 30-, and 40-per cent-castor oil modifications filled with 40 per cent of asbestos fiber. Motor Firing B would be expected to give higher char rates than A because of its higher
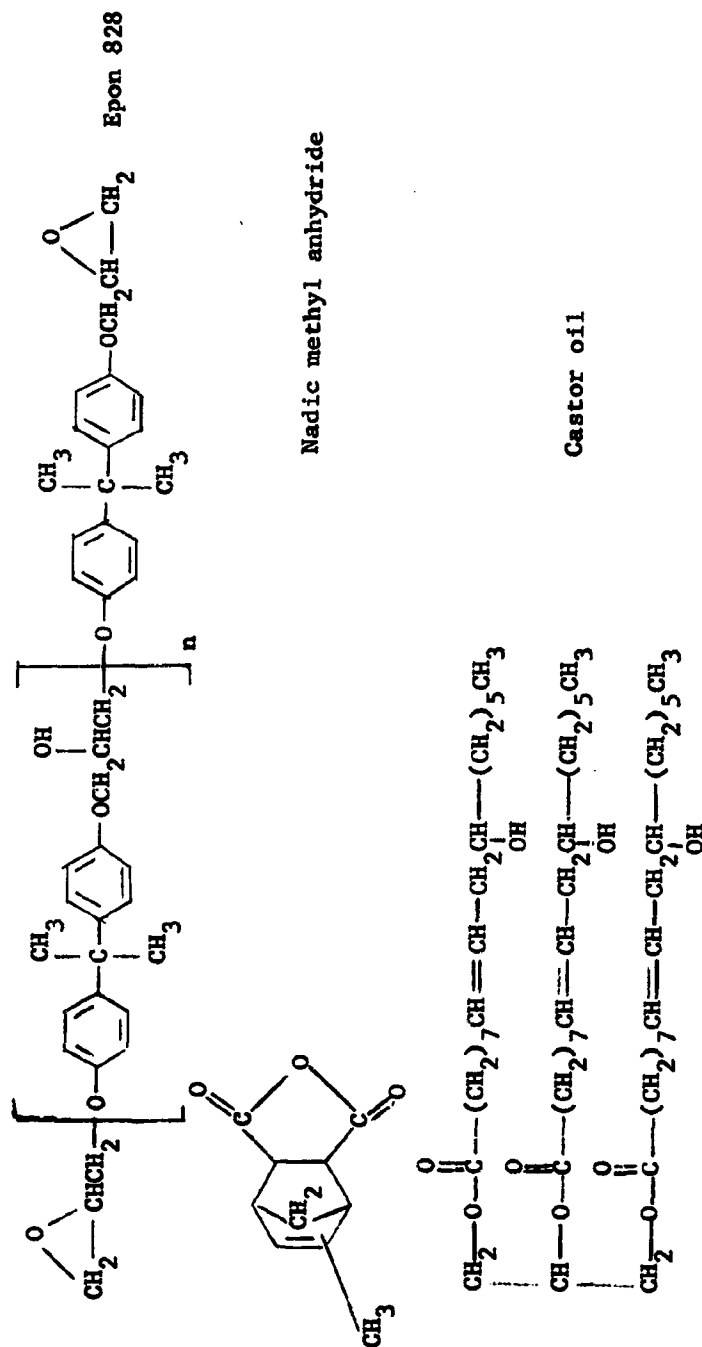
Figure 4. Ingredients Used in the Castor Oil-Modified, Epoxy-Anhydride Resin

55

TABLE II

Effect of Castor Oil Concentration on the Char Rates of
40-Per Cent Asbestos-Fiber-Filled, Castor Oil-Modified,
Epoxy-Anhydride Resins Tested in Static Motors

Castor Oil (in resin)	Char Rate[a] (mil/sec)
Motor Firing A	
0	4.0^b
10	5.4^b
20	3.6^b
30	3.2^b
Motor Firing B	
0	5.1^c $(4.0)^d$
40	3.0^c $(2.4)^d$

---

a. Materials evaluated in the nozzle approach section.

b. These materials were tested in the same motor. Propellant flame temperature was 6500°F, pressure 400 psi, firing time 50.2 sec.

c. These materials were tested in the same motor. Propellant flame temperature was 6500°F, pressure 777 psi, firing time 43.6 sec.

d. Char rates determined by adjusting the 0.0-per cent-castor oil specimen in Motor B to 4.0 mil/sec (the char rate for the identical material in Motor A) and proportionally changing the char rate for the 40-per cent-castor oil specimen.

pressure and shorter firing time. This accounts for the two different char rates obtained for the identical material (0.0 per cent of castor oil) tested in both motors. By comparing the adjusted char rates of motor B with the char rates of motor A, it is evident that the insulation performance of the 40-per cent-castor oil specimen is significantly improved over the 30-per cent-castor oil specimen by more than the 0.2 mil/sec indicated by the measured char rates.

Since the density of these formulations is a function of the asbestos content of the resin, the optimum loading for maximum insulation performance (based on char rate <u>and</u> density) was determined for the 40-per cent-castor oil modification. In Table III are reported the motor test results. The char rate for the sample with 20 per cent of asbestos is probably in error and would be expected to be closer to 2.5 than the 1.6 value actually recorded. The best performance is therefore shown by the sample containing 40 per cent of asbestos.

Since the type of filler used with a particular resin may significantly effect the insulation performance and density, we have evaluated other fillers for our more promising resins. In Table IV are shown the char rates of the 40-per cent-castor oil modification with various fillers. Although sample (1) looks very good with a char rate 1.1 mil/sec, the extensive swelling and voids in the remaining uncharred layer of the tested specimen does not allow an accurate evaluation of the performance of the material based only on char rate. By replacing the 10 per cent of asbestos powder with 20 per cent of asbestos fiber (2), swelling and voids in the uncharred layers of the tested specimen were eliminated. The char rate of 2.4 mil/sec for this filler system represents an improvement in performance over that of sample (4) with a char rate of 2.6 mil/sec that contains only asbestos fiber as a filler. However, since the asbestos and the potassium oxalate have approximately the same density, this property is unchanged. By using the Eccospheres Si, (hollow silica microspheres) as a filler, a material of very low density (0.69 gm/cc) is obtained. Although the char rate is high (5.0 mil/sec) the char rate density factor is still low. An Eccosphere-asbestos fiber-potassium oxalate composite filler is being studied.

A second important area of our work is flexible phenolic resins. Completely polymerized phenolic resins are highly cross-linked, completely insoluble, and infusible materials. But if the chain length between phenolic molecules is increased and/or the amount of cross-linking is reduced, improved flexibility can be expected. In Figure 5 are shown the ingredients used in the preparation of a modified phenol-formaldehyde resin. The formaldehyde is condensed with the phenol to produce a resol whose structure may be represented as shown in Figure 5. This A-stage, phenol-formaldehyde prepolymer can be chain extended and cured by a large number of materials capable of reacting with the hydroxyl groups (e.g., diacids, diisocyanates, glycols). Syl Kem 90, a silicone diepoxide, was investigated first. The ultimate elongations and the tensile

57

TABLE III

Effect of Asbestos Content on the Char Rate of the
40-Per Cent Castor Oil-Modified, Epoxy-Anhydride Resin as
Determined in Static Motor Test[a]

Asbestos Fiber Content (per cent)	Density (gm/cc)	Char Rate (mil/sec)	Char Rate × Density
13	1.22	2.5	3.0
20	1.24	1.6	2.0
30	1.33	2.6	3.5
40	1.45	1.9	2.8
50	1.54	1.9	2.9

a. All specimens tested in same motor in the convergent section.
Propellant flame temperature 5600°F, pressure 700 psi, firing time
92.4 sec.

TABLE IV

Effect of Various Fillers on the Char Rate of the
40-Per Cent-Castor Oil-Modified, Epoxy-Anhydride Resin
as Determined in Static Motor Tests

Filler	Density (gm/cc)	Char Rate (mil/sec)	Char Rate × Density
(1) 10% asbestos powder 20% potassium oxalate	1.32	1.1[a]	1.3
(2) 20% asbestos fiber 20% potassium oxalate	1.46	2.4[b]	3.5
(3) 40% Eccospheres Si	0.69	5.0[b]	3.4
(4) 50% asbestos fiber	1.54	2.6[b]	4.0

a. Convergent section, propellant flame temperature 6500°F, pressure 400 psi, firing time 34.8 seconds.

b. Convergent section, propellant flame temperature 5600°F, pressure 773 psi, firing time 61.6 seconds.
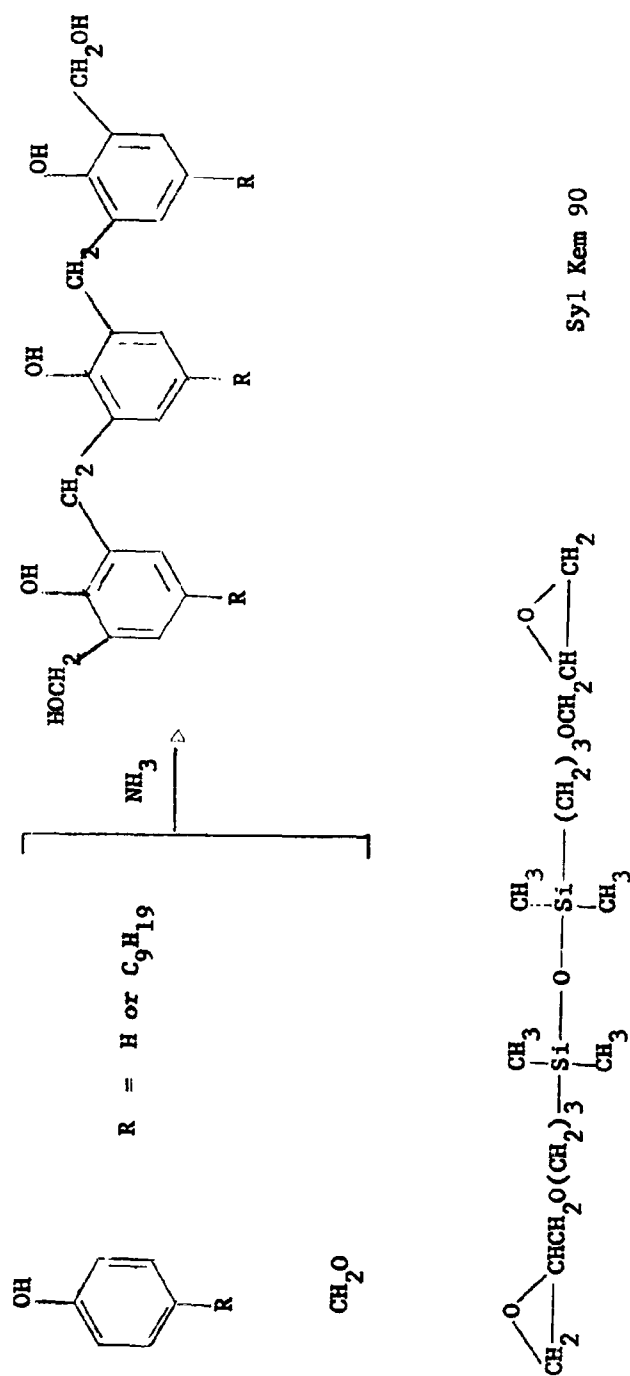
Figure 5. Ingredients Used in the Flexible Phenolic Resin

60

strengths of the phenol- and nonylphenol-formaldehyde resins modified with various amounts of Syl Kem 90 (unfilled) are shown in Figures 6, 7, and 8.

In Table V are reported the motor test data for the phenol-formaldehyde prepolymer modified with varying amounts of Syl Kem 90 and filled with 45 per cent of asbestos. With increasing phenol-formaldehyde resin, the char rate decreases but the density increases. Since the 50:50 ratio of resin to modifier showed best performance, this formulation was investigated with other fillers; the motor test results are reported in Table VI. The asbestos fiber-potassium oxalate composite, with lowest char rate and density, appears to be the best filler.

In summary, flexible epoxy and phenolic resins with very good insulation performance in static firings of solid porpellant motors have been prepared. Further work in the development of these and other flexible resins is continuing.
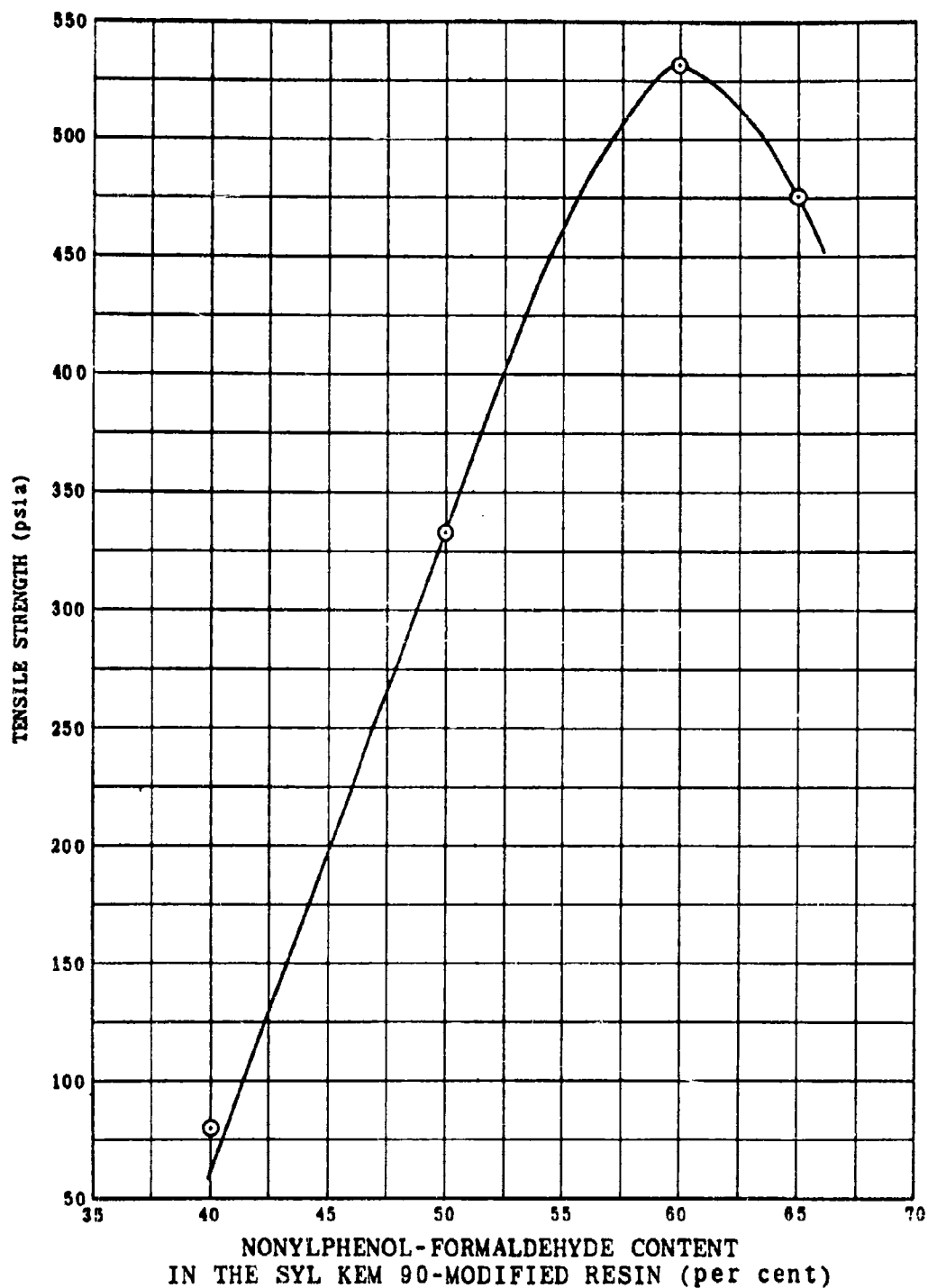
Figure 6. Effect of Resin Composition on Tensile Strength for the
Nonylphenol-Formaldehyde-Syl Kem 90 Formulations.
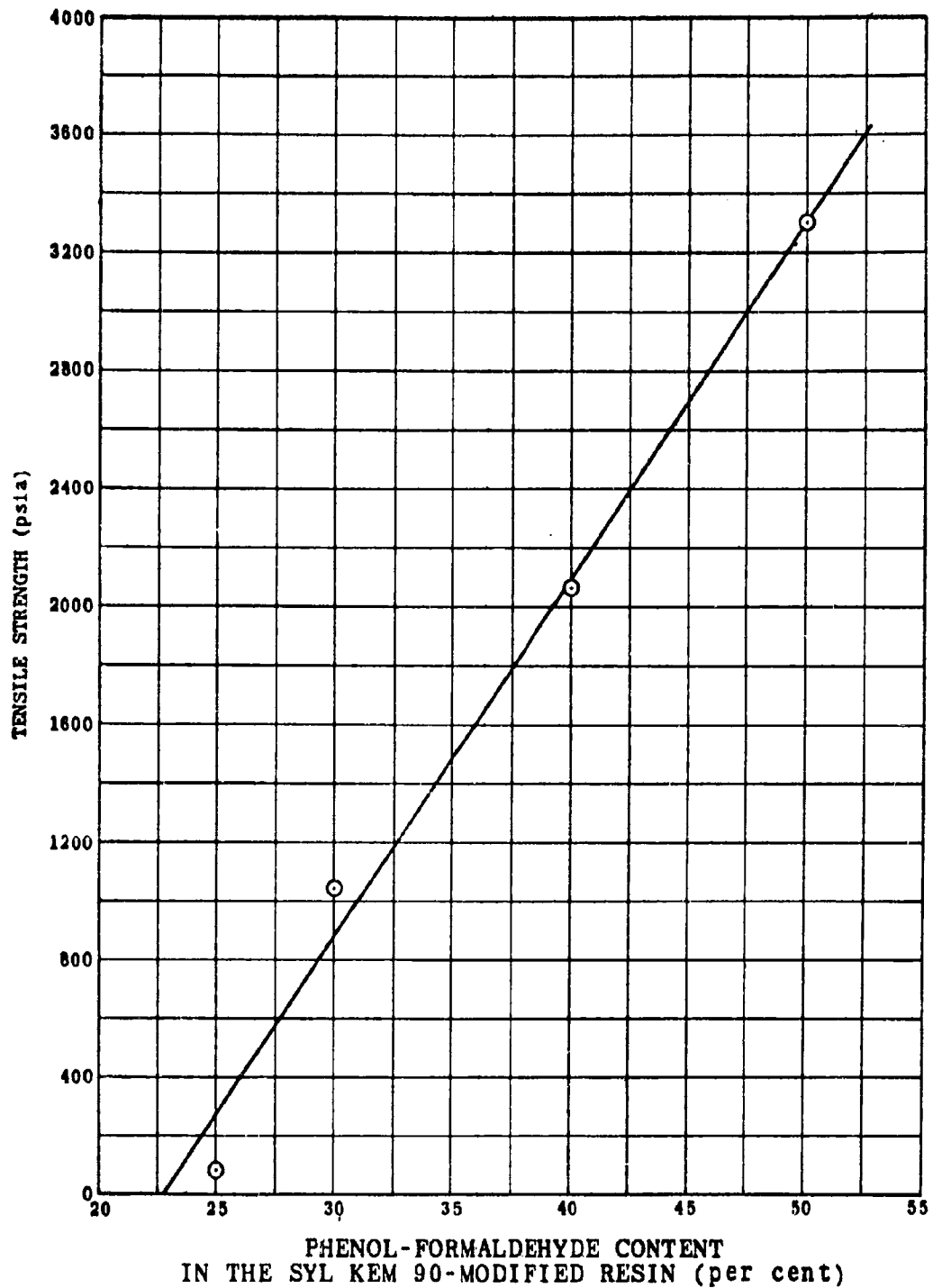
Figure 7. Effect of Resin Composition on Tensile Strength for the Phenol-Formaldehyde-Syl Kem 90 Formulations.
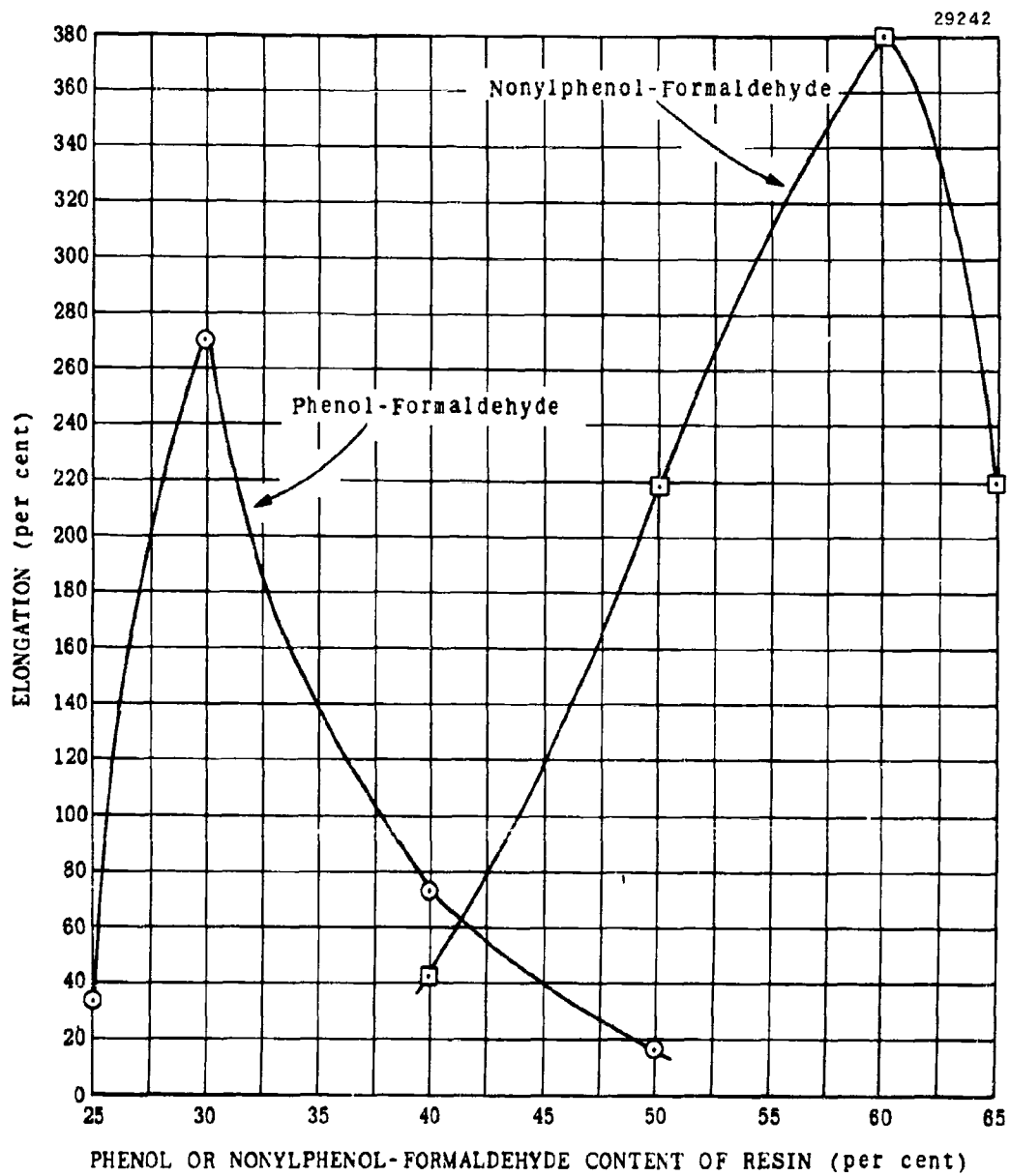
Figure 8. Effect of Resin Composition on Elongation for the Phenol and
Nonylphenol-Formaldehyde-Syl Kem 90 Formulations.

TABLE V

Static Motor Testing of 45-Per Cent-Asbestos-Filled,
Phenol-Formaldehyde Prepolymer Modified
with Varying Amounts of Syl Kem 90

Phenol-Formaldehyde Syl Kem 90 ratio	Density (gm/cc)	Char Rate[a] (mil/sec)	Char Rate × Density
50:50	1.52	2.6	4.0
40:60	1.49	3.3	4.9
30:70	1.45	3.6	5.2
20:80	1.39	4.6	6.4

a. Convergent section; propellant flame temperature 5600°F; pressure 749 psi; firing time 30.2 seconds.

TABLE VI

Static Motor Testing of the Syl Kem 90-Modified
Phenol-Formaldehyde Prepolymer (50:50 Ratio)
Containing Various Fillers

Filler	Density (gm/cc)	Char Rate (mil/sec)	Char Rate × Density
45% asbestos fiber	1.52	2.6[a]	4.0
22.5% asbestos fiber 22.5% potassium oxalate	1.50	2.1[b]	3.1
45% potassium oxalate	1.50	5.2[c]	7.8

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a. Convergent section, propellant flame temperature 5600°F,
pressure 749 psi, firing time 30.2 seconds.

b. Convergent section, propellant flame temperature 5600°F,
pressure 713 psi, firing time 68.1 seconds.

c. Convergent section, propellant flame temperature 6500°F,
pressure approximately 700 psi, firing 46.0 seconds.

FLEXIBLE MOTOR CASE INSULATORS (C)

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ABSTRACT

The U.S. Rubber Company is under contract (NOrd-16788) with Department of the Navy, Bureau of Naval Weapons, for development of superior flexible motor case insulators. The major portion of the effort is being directed specifically towards insulators for the POLARIS missile; however, recently the Navy has asked us to provide insulation serviceable at ambient temperature of -65°F to +170°F.

Two broad classes of flexible insulator materials developed show great promise and are candidate materials for motor case linings for POLARIS A3 second stage. These two classes are composites of (1) elastomer-resin-low temperature decomposing filler, and (2) elastomer-fiber.

Both classes of chamber insulation described are flexible, low density compositions which exhibit char and erosion rates far superior to currently used flexible motor case insulation. In addition, they have char and erosion rates equal or superior to the asbestos-phenolic insulation currently used in the high erosion aft motor areas. This makes possible fabrication of motor case insulators from a single flexible material, thus eliminating the rigid high density insulation normally used in the aft pan or the motor case. Indicated weight savings for the entire insulator linings are in the range of 40 to 60%. These insulations are undergoing qualification and thickness requirement evaluations in full-scale POLARIS A-3 second stage motors at Allegany Ballistics Laboratory.

Some of the elastomer-fiber blends also have indicated ambient temperature capability of -65°F to +170°F, although this range has not been completely substantiated. This indicated broad temperature capability should provide the same advantages for motor insulations of ship and air launched missiles.

The mechanism of protection is reasonably well understood. Extrapolation indicates promising insulations for other very high erosion services while maintaining low density and flexibility.

67

ADHESION STUDIES ON LINER AND PROPELLANT

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The loading of solid propellant rocket motors consists of lining the case with a thin rubbery material and then casting the propellant into this lined case. The liner is applied by spraying or doctoring a viscous liquid material capable of being heat cured to the desired rubbery characteristics. The propellant is then added and again cured by heating. This process gives rise to two interfaces in which good adhesion is mandatory, the liner to case interface and the liner to propellant interface. This study was initiated to determine causes of failure of liner to case and liner to propellant bonds in case bonded solid propellant rocket motors. Obviously, the first problem encountered was to determine what type of failure was being experienced--adhesive or cohesive. Adhesive failure, the separation of the liner from the case or the propellant from the liner, presents one type of problem, whereas cohesive failure, the actual breaking of the material, gives rise to another type. Another problem related to adhesion is the wetting phenomenon, how well does the adhesive wet the surface of the adherend? These two problems are discussed separately.

Lasoski and Krause [1] define the work of cohesion and the work of adhesion as:

$$Wcoh = 2\gamma p$$

$$Wadh = \gamma m + \gamma p - \gamma p/m$$

where the γ's are surface free energies of the metal (m), polymer (p) and polymer/metal interface (p/m).

For cohesive failure to occur, Wcoh $<$ Wadh thus

$$\gamma p + \gamma p/m < \gamma m$$

for adhesive failure, Wadh $<$ Wcoh and $\gamma p + \gamma p/m > \gamma m$

Since the surface free energies of metals are much higher than those of organic polymers, the relationship $\gamma p + \gamma p/m < \gamma m$ should hold even though the value of $\gamma p/m$ is likely to be high.

The "limiting tensile adhesion" method of Manson and Krause[2] was chosen to determine the type of failure. This method consists of bonding two surfaces together with varying thicknesses of adhesive and determining the force required to pull them apart.

A plot of the force versus the thickness when extrapolated to zero thickness is the "limiting tensile adhesion", and if the bond is broken by only cohesive failure, this value should be the same as the tensile strength of the adhesive itself.

The limiting tensile adhesion was determined for three liner compositions. These are J-1, a polysulfide based liner, and P-5 and P-8 which are based on the elastomeric binder used in the HA propellants. The apparatus used was a set of blocks shown in Figure 1. The blocks were thoroughly degreased, the liner placed between them and cured. The blocks were then measured to determine the thickness of the liner and pulled apart using an Instron machine.

Figure 2 shows a least squares plot of the data obtained with J-1 liner, Figure 3 those data obtained with P-5, and Figure 4 those from P-8.

The limiting tensile adhesions in all cases approach or surpass the tensile strength of the liner itself showing that the failure is cohesive and that there is no problem of adhesion of liner to metal, providing the surfaces are clean. Table I shows the tensile strengths and limiting tensile adhesions of these liners as well as the 95% confidence interval of the limiting tensile adhesion.

Extension of these criteria to the propellant-liner bond results in

$$Wcoh_{pr} = 2 \gamma pr$$

$$W coh_1 = 2\gamma 1$$

when $Wcoh_{pr} < Wcoh_1$, failure will occur in the propellant if the value of Wadh is greater than either Wcoh value. Making the assumption that the above inequality is descriptive of the prevailing situation, the equations must take into consideration for adhesive failure $Wcoh_{pr} < Wadh$, not $Wcoh_1 < Wadh$, which would prevail if the liner were weaker than the propellant.

Wadh = $\gamma pr + \gamma 1 - \gamma pr/1$ defines the work of adhesion in this instance. To have adhesive failure occur

$$2\gamma pr > \gamma pr + \gamma 1 - \gamma pr/1$$

$$\gamma pr > \gamma 1 - \gamma pr/1$$

$$\gamma pr/1 > \gamma 1 - \gamma pr$$

The test blocks used in the liner-metal adhesion study were modified for use in this test. Figure 5 shows the modification. The liner propellant system used was P-8 - TPH-8041. The binder system in TPH-8041 is a polybutadiene material identical to that used in P-8 liner. The results of this study are shown in figure 6. A least squares analysis of these data shows no correlation of tensile with thickness and no conclusions have been drawn from them although it appears from visual inspection of the test blocks that this is again a case of cohesive failure.

Among the problems associated with adhesion is the wetting of surfaces by the uncured adhesive. Both wetting of steel and of ammonium perchlorate was studied. Contact angles were determined by use of a microscope. The contact angles of the three liners with H-11 steel are shown in Table II. As can be seen from the table, P-5 liner has the smallest contact angle and thus wets the surface of H-11 steel better than either of the others. This is borne out by the difficulty in cleaning test blocks which have been used with P-5 liner.

The contact angles of several mixtures with ammonium perchlorate were measured. Table III shows the results of this study. It can be seen that wetting agents have little or no effect on the wetting of ammonium perchlorate by the HA-curing agent mixture but that treatment of the surface by tricalcium phosphate and vacuum drying the ammonium perchlorate improves the wettability of the oxidizer by the fuel-binder system. Wetting agents in conjunction with tricalcium phosphate also improve the wettability.

70

TABLE I

Tensile Strengths and Limiting Tensile Adhesion of Liners

Liner	Tensile Psi	LTA Psi	95% Conf. Interval
P-5	270	308	±50
P-8	340	344	±21
J-1	430	428	±39

TABLE II

Contact Angles of Liner with H-11 Steel

	Polished	Unpolished
J-1	33°39'	40°03'
P-5	10°48'	15°01'
P-8	23°15'	30°30'

TABLE III

Contact Angles of Fuel-Binder Mixtures with Ammonium Perchlorate

	Air Dried	Vacuum Dried	Air dried With TCP*	Vacuum Dried with TCP*
HA-Curing Agent	22°57'	15°00'	17°38'	12°12'
HA-Curing Agent Victawet 12	20°24'	19°45'	13°44'	
HA-Curing Agent Isothan OL-T	21°38'	21°59'	9°44'	

*Tricalcium phosphate dusted on crystal.

Figure I

Test Block for Limiting Tensile Adhesion
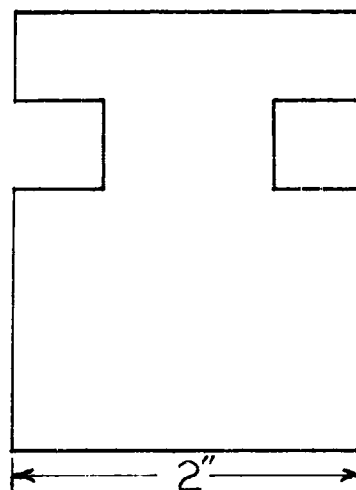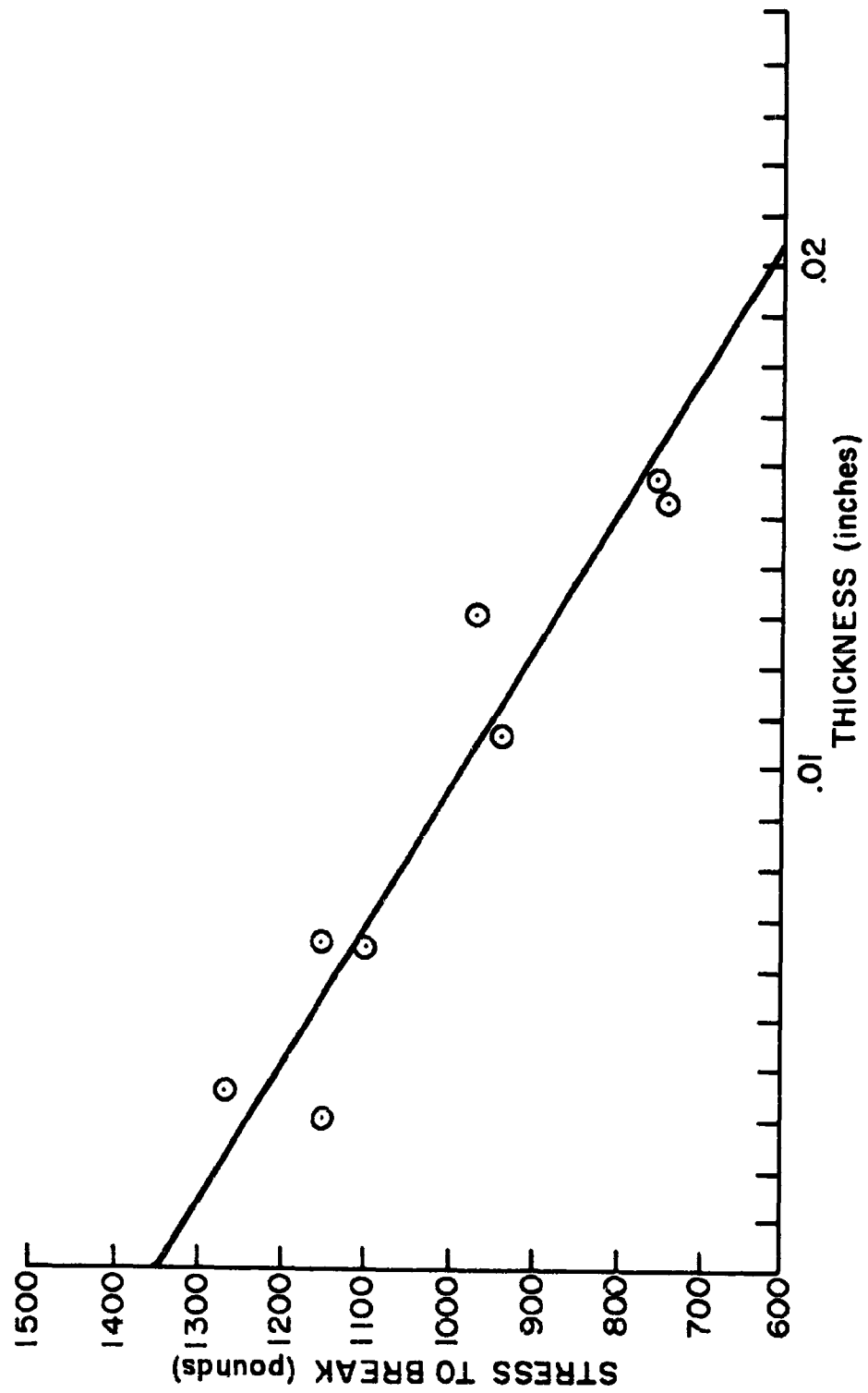
FIG. 2. J-1 LINER LIMITING TENSILE ADHESION.
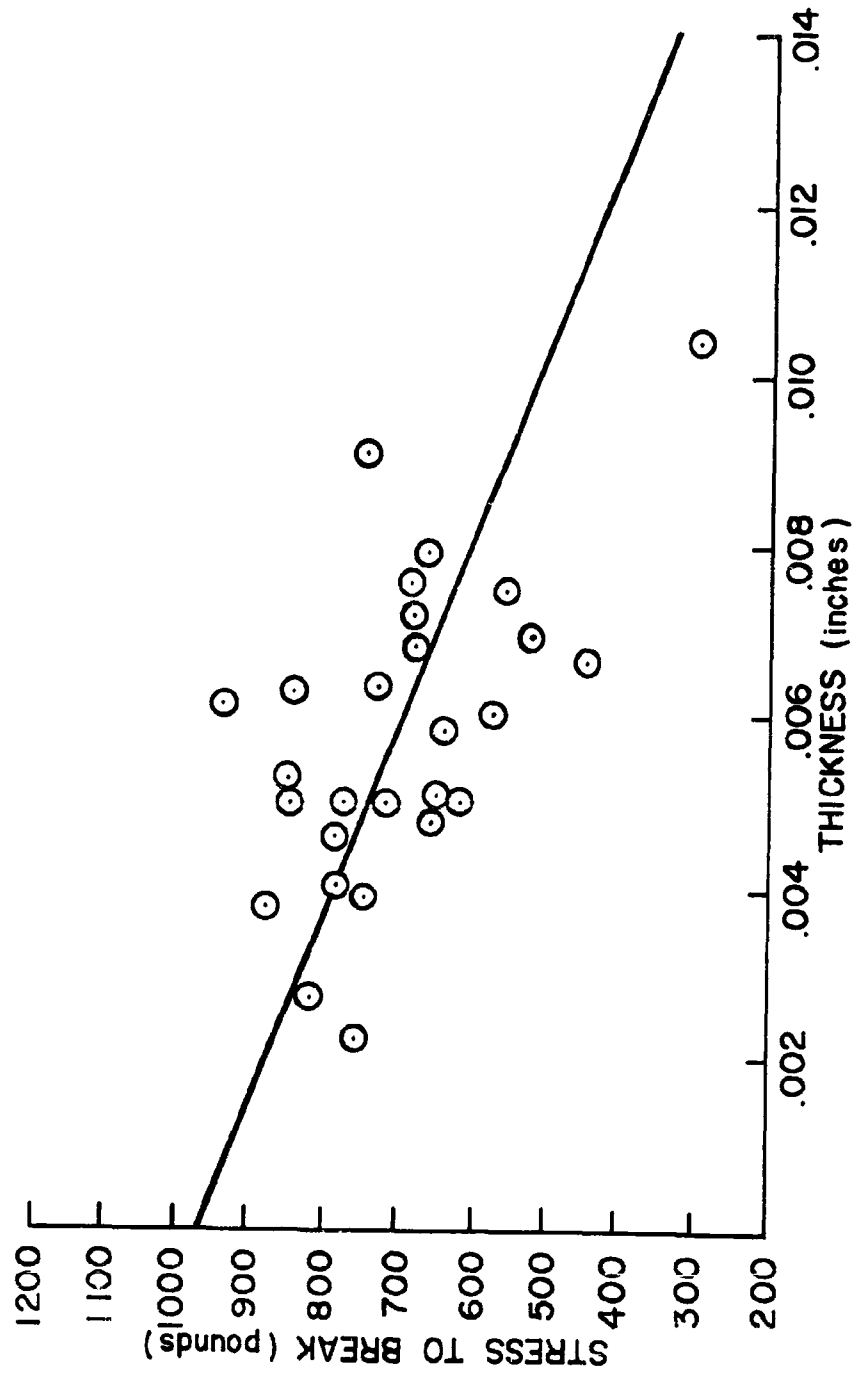
FIG. 3.   P-5 LINER LIMITING TENSILE ADHESION
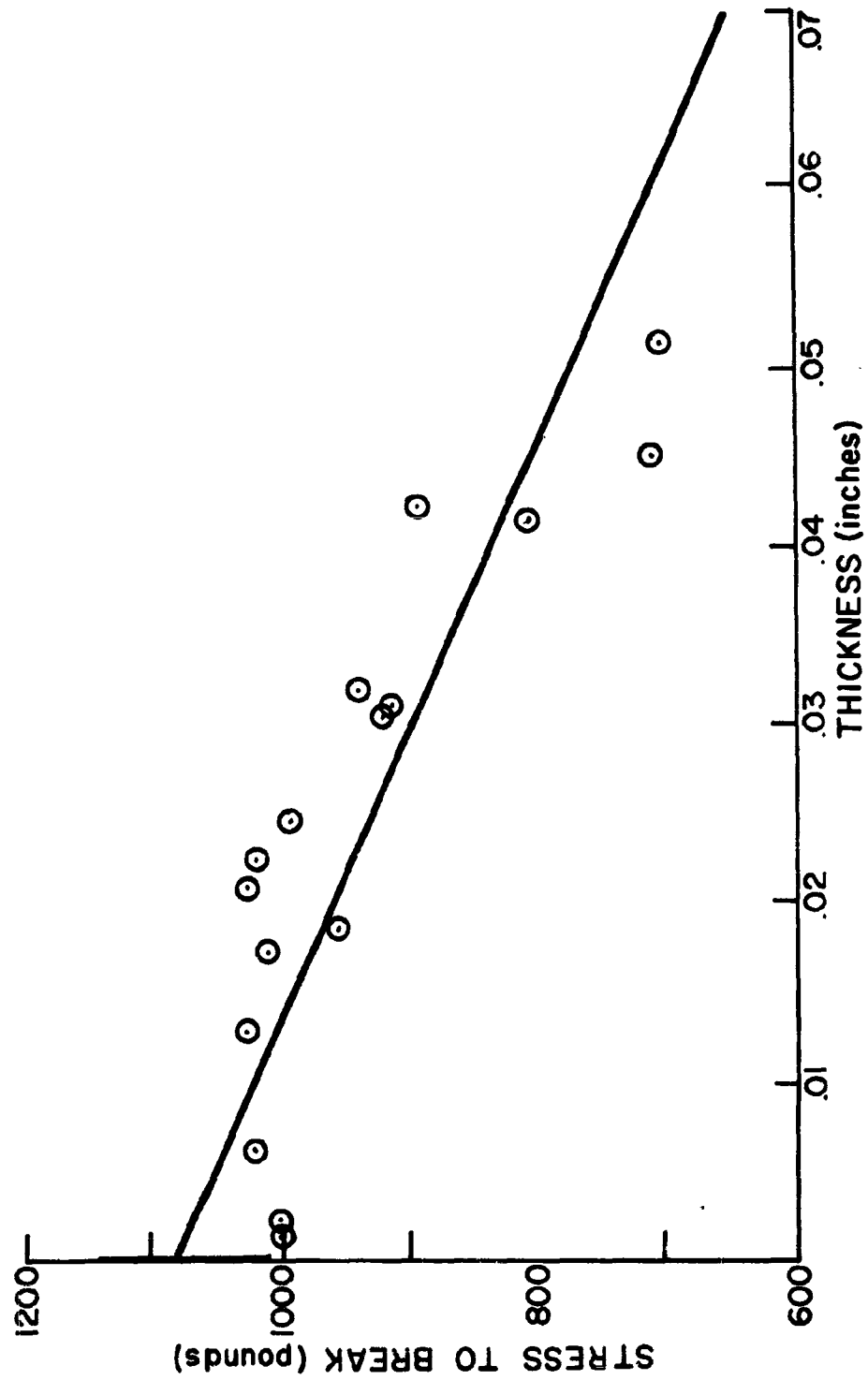
FIG. 4. P-8 LINER LIMITING TENSILE ADHESION.
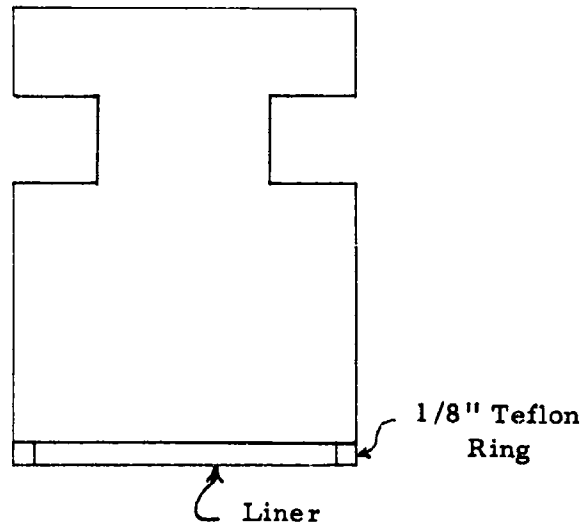
Figure 5

Test Block Modified
for Propellant
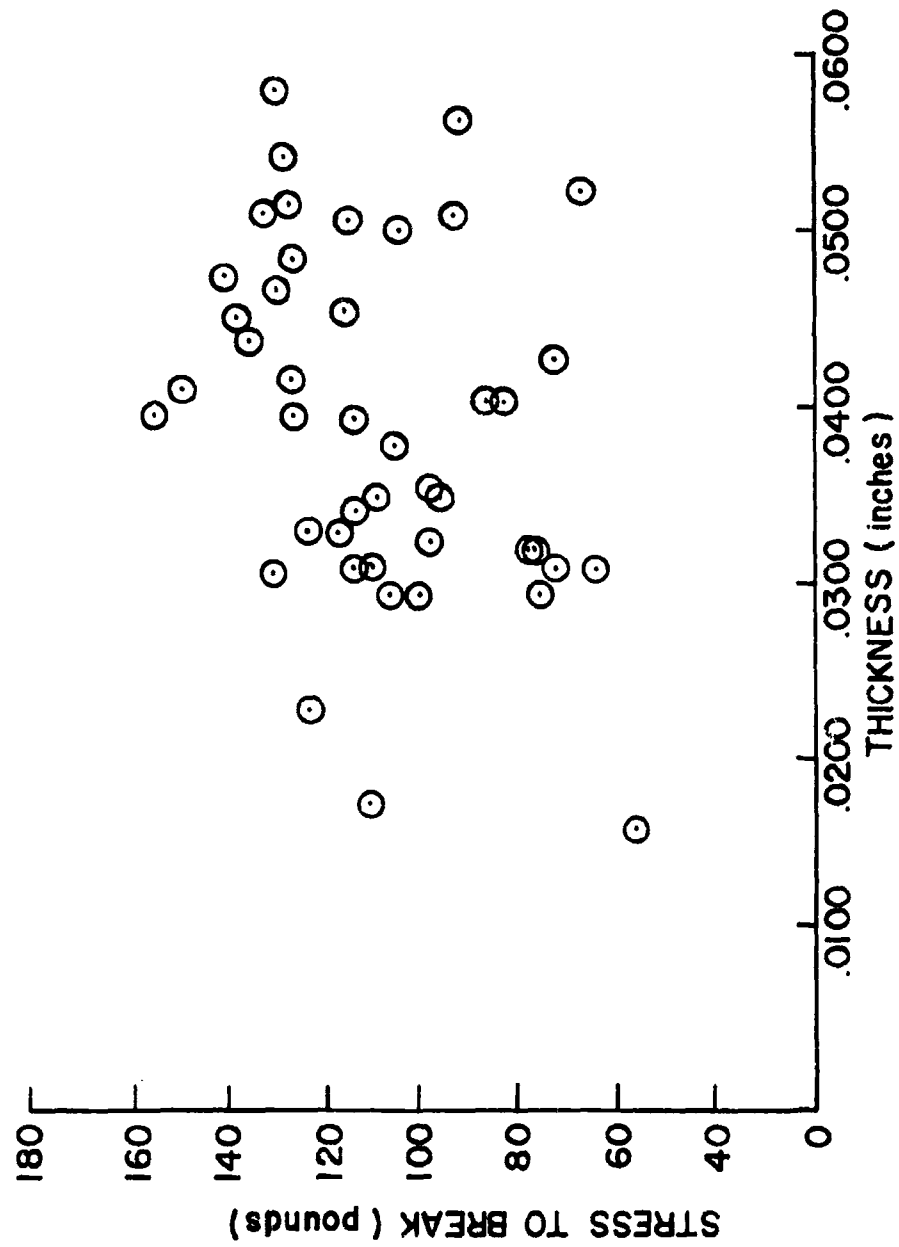
FIG. 6. ADHESION OF TP-H804I PROPELLANT TO P-8 LINER.

Much work has been done with treating surfaces to improve adhesion. This work indicates that such treatment may not be necessary and, in fact, may be deleterious. The prime consideration should be a surface which is clean of all low tensile strength materials such as grease. Even adsorbed air can act as an impurity; thus, good wetting as shown by low contact angles is important.

Bikerman[3] has stated that no case of true adhesive failure has been found. He claims that all instances of inspected adhesive failure may be attributed to an impurity on the surface of the adherend or in the adhesive itself which forms a layer of low tensile strength between the adhesive and the adherend.

In summary, the three liners subjected to this study show good adhesion to steel; in no case has adhesive failure been observed. This is shown by the limiting tensile adhesion approaching or surpassing the measured tensile strengths of the liner. A similar study on a liner-propellant bond was inconclusive; however, visual inspection indicates cohesive failure.

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CRYSTALLINITY IN SOLID
PROPELLANT BINDERS (C)

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ABSTRACT

Solid propellants for Army rockets are expected to retain rubbery properties at temperatures ranging down to those of Arctic weather. Since certain elastomers are known to crystallize at low temperatures, an investigation has been made of the low temperature behavior of solid propellants which contain elastomeric binders. Methods employed were chiefly dilatometric measurement of volume change and measurement of mechanical property changes. In some cases x-ray diffraction studies also proved useful. Data gathered from this work will be presented, and the low temperature properties of several propellants willbbe discussed.

ELASTOMERIC AND COMPLIANT MATERIALS FOR CONTACT WITH LIQUID ROCKET FUELS AND OXIDIZERS

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The need of greater specific impulse for the propulsion systems of advanced aerospace craft and missiles has been accompanied by increasingly severe materials compatibility problems. The fuels and oxidizers of requisite energetic qualities are generally chemically reactive with organic materials of construction. It is desirable to prepare such end items as seals, gaskets and flexible connectors from elastomeric polymers due to their simplicity and low weight penalty. However, elastomers have proved to be susceptible to attack by the more energetic propellant fuels and oxidizers. Hence, research on elastomeric and compliant materials resistant to hydrazine-type fuels, nitrogen tetroxide and fluorine-containing oxidizers has been needed.

Several approaches toward developing elastomeric and compliant materials compatible with these liquids were investigated. Commercially available polymers and small quantities of experimental polymers were subjected to formulation and evaluation studies. Resin coated elastomers were prepared and their compatibility with the various fuels and oxidizers was determined. Techniques of encapsulating elastomers with thin coatings of metals were investigated for compatibility with such oxidizers as chlorine trifluoride

Compatibility with Hydrazine Type Fuels

Previous literature had indicated that hydrocarbon elastomers such as butyl rubber, cis-1,4-polybutadiene and Hydropol (hydrogenated polybutadiene) are best suited for hydrazine-type fuel application (1, 2, 5). The present study quantitatively evaluated these elastomers, as well as others, for compatibility in specific fuels, e. g. , hydrazine-unsymmetrical dimethyl hydrazine

(UDMH) blends, monomethylhydrazine (MMH), and mixed hydrazine
fuels (MHF-1 and MHF-4). In addition, these compositions were
evaluated dynamically as O-ring seals in the specific fuel.

The formulations of the compositions studied are shown
in Table I. The elastomers studied were Hydropol (hydrogenated
polybutadiene), cis-1,4-polybutadiene, butyl and ethylene-propylene
rubber (EPR). Compatibility data were obtained after immersion in
50/50 hydrazine/UDMH at room temperature and 160° F. Although
all the compositions studied showed excellent compatibility in
hydrazine/UDMH, EPR composition 132 showed no change in physi-
cal properties after 30 days total immersion at 160° F (Tables II
and III). The control samples for the above data were also aged
30 days at 160° F but without fuel immersion.

The method of obtaining volume swell data, and con-
sequently the early hydrazine compatibility data reported in the
literature and also obtained at these laboratories are in question.
Hydrazine-type fuels are miscible in all proportions with water,
hence, the operation of weighing the swollen samples in water after
immersion as is called for by ASTM D 471-57T, could result in
low volume swell data. The high volatility of some of the hydrazine-
type fuels could also result in fallacious swell data using this meth-
od of measurement. In these laboratories ASTM D 1460-60,
"Change in Length of an Elastomeric Vulcanizate Resulting from
Immersion in a Liquid" has been used for obtaining volume swell
data. In this test the change in length of the sample is measured
while still immersed by use of graph paper background. Knowing
the original sample dimensions the change in length can be related
to a volume change. Based on method D 1460-60, the volume
swells of butyl compositions in hydrazine/UDMH and in MMH and
that of cis-1,4-polybutadiene in the former fuel may be marginal
with regard to the specifications. The volume change of the
EPR-132 formulation is low when immersed in any of the hydra-
zine-type fuels.

Tables IV and V summarize the physical properties of the
various vulcanizates after immersion in MMH, MHF-1 and MHF-4
for 7 days at 160° F. Once again the hydrocarbon polymers tested
are all compatible with these fuels with the EPR-132 formulation
showing the best overall compatibility.

The volume swell tests were carried out by using a modi-
fied version of ASTM D 1460-60. A rectangular specimen 50 mm
long, 1.6 mm wide, and 1.9 mm thick was placed in a glass tube

TABLE I

FORMULATIONS FOR COMPATIBILITY STUDIES
IN MIXED HYDRAZINE FUELS

Formulation No.	32	33	34	35	121	132
Hydropol V	80	---	---	---	---	---
Hydropol TP	20	---	---	---	---	---
Cis-4-Polybutadiene	---	---	---	100	---	---
Butyl 218	---	100	100	---	100	---
EPR	---	---	---	---	---	100
Polyethylene	---	---	25	---	---	---
Statex R (HAF)	40	75	75	50	65	50
Stearic Acid	2	---	---	1	---	---
Zinc Oxide	5	5	5	5	5	---
Sulfur	1.75	---	---	2.5	---	---
DiCup 40C	---	---	---	---	---	10
Methyl Tuads	0.75	---	---	0.4	---	---
Flexamine	0.1	---	---	---	---	---
Amberol ST 137	---	12	12	---	50	---
Dioctyl Sebacate	---	10	10	---	---	---
Hypalon 20	---	5	5	---	5	---

Green

TABLE II

PHYSICAL PROPERTIES OF VULCANIZATES DEVELOPED FOR COMPATIBILITY WITH 50/50 HYDRAZINE/UDMH, ROOM TEMPERATURE IMMERSION

Base Elastomer	Formulation No.	Immersion Time, days	Tensile, psi	Elongation, %	Shore A, points
Specs after Exposure			500 min	100-600	10-90
Butyl	34	Original [1]	1440	210	65
		1	1610	275	64
		7	1370	185	62
Cis-4-PB	35	Original [1]	1400	330	67
		1	1590	325	61
		7	1700	325	61

----

(1) Original Properties before fuel immersion.

Green

TABLE III

PHYSICAL PROPERTIES OF VULCANIZATES DEVELOPED FOR COMPATIBILITY WITH 50/50 HYDRAZINE/UDMH, 160°F IMMERSION

Base Elastomer	Formulation No.	Immersion Time, days	Tensile, psi	Elongation, %	Shore A, points	Volume Change %(3)
Specs after exposure			500 min	100-600	40-90	30 max
Butyl	34	Control (1)	1770	310	84	
		1	1730	610	80	(7)
		7	1740	590	75	(18)
Cis-4-PB	35	Control (1)	1440	450	70	
		1	1370	485	64	(12)
		7	1320	475	62	(23)
Butyl	121	Control (1)	1620	200	90	
		7	1300	200		
		Control (2)	1630	175		
		30	1900	175		44(25)
EPR	132	Control (1)	1980	400	60	
		7	1850	400		
		Control (2)	1940	425		
		30	2040	425		16(17)

(1) Aged 7 days in 160°F without fuel immersion

(2) Aged 30 days at 160°F without fuel immersion

(3) ASTM D 1460-60; figures in parenthesis are according to ASTM D 471-57T

84

TABLE IV

PHYSICAL PROPERTIES OF VULCANIZATES DEVELOPED FOR COMPATIBILITY
WITH MMH, 7 DAYS/160°F IMMERSION

Base Elastomer	Formulation No.	Fuel	Tensile, psi	Elongation %	Shore A, points	Volume (2) Change %
Specs after exposure			500 min	100-600	40-90	30 max
Butyl	34	Control (1)	1770	310	84	
		MMH	1500	280	73	26
Cis-4-PB	35	Control	1440	450	70	
		MMH	1630	125	77	9
EPR	132	Control	1980	400	60	
		MMH	1730	425	58	18

(1) All controls aged 7 days/160°F without fuel immersion

(2) ASTM D 1460-60

TABLE V

PHYSICAL PROPERTIES OF VULCANIZATES DEVELOPED FOR COMPATIBILITY
WITH MHF-1 AND MHF-4. 7 DAYS/160°F IMMERSION

Base Elastomer	Formation No.	Fuel	Tensile, psi	Elongation, %	Shore A, points	Volume[2] Change, %
Specs after exposure			500 min	100-600	40-90	30 max
Butyl	34	Control [1]	1770	310	84	--
		MHF-1	1640	280	87	8
		MHF-4	1580	310	82	9
Cis-4-PB	35	Control	1440	450	70	--
		MHF-1	1600	125	75	8
		MHF-4	1830	125	78	9
EPR	132	Control	1980	400	60	--
		MHF-1	1830	325	58	5
		MHF-4	1750	340	57	9

(1) Aged 7 days 160°F without fuel immersion

(2) ASTM D 1460-60

10 mm in outside diameter. A glass rod, 7.5 mm in diameter and 2 cm. in length, with square cut ends was placed on the bottom of each tube. Enough test liquid was placed in the tube to reach a level double the test specimen length. Specimens were cut both with and against the grain. Using this technique, it was possible to obtain volume swell measurements on each specimen at regular intervals, without removing the specimens from the test liquid, by measuring the length before immersion, and at the desired time intervals. The figure ΔL is then related to the corresponding change in volume (ΔV), expressed as a percentage according to ASTM.

The low temperature flexibility of compounds 34 and 35 was evaluated by subjecting them to a 180° bend at $-70^{\circ}F$; neither compound showed any signs of cracking. The former compound stiffened slightly but the latter showed no noticeable stiffening. EPR formulations are reported to have excellent low temperature properties (7). The compression set data for these compounds according to ASTM D 395 Method B, 22 hours at $158^{\circ}F$ are listed below:

Compound	Compression Set, %
34	26
35	17
121	29
132	15

One of the objectives of the program was to dynamically evaluate the developed compositions as O-ring seals for hydrazine-type fuel application. The Thiokol - RMD dynamic O-ring tester shown in Figure I was used for evaluation. The tester consists of a piston cylinder combination with two O-rings located on the piston as shown in the figure. The piston is cycled in the cylinder at a rate of 3600 cycles per hour with a stroke of 1/2 inch. The fuel or oxidizer under test is sealed between the two O-rings. Additional propellant is stored in a reservoir above the tester and pressurized from a nitrogen cylinder through a three-way valve. The entire apparatus fits into a temperature control box so that the O-rings can be tested over a range of operating temperatures and pressures. A photograph of this tester is shown in Figure 2.

Tables VI and VII summarize the data obtained with the O-ring tester when cycled at 3600 cycles per hour and at -60 to $160^{\circ}F$. Although the Hydropol O-rings functioned well they were considered too stiff for practical application. The use of poly-ethylene in composition 34 as compared to composition 33,

87

Figure 1 - Assembly Drawing of O-ring Tester

PROTECTIVE DOOR

SHATTERPROOF GLASS WINDOW

500 PSi

CHECK VALVE

SAFETY SHOWER

RELIEF VALVE

TEMP CONTROL CABINET

TEST UNIT

AIR PISTON

ALUMINUM TRAY

O-RINGS

DRAINS

FUEL

N₂

N₂

N₂
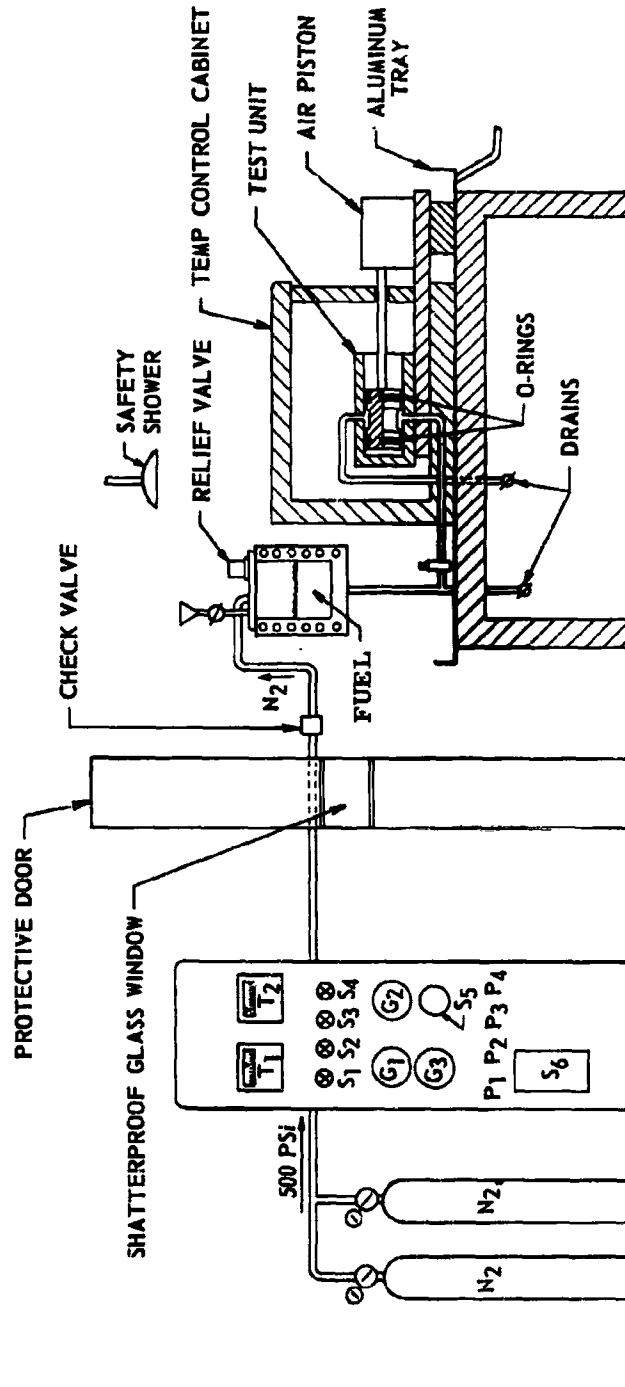
T_1 TEMPERATURE CONTROLLER, OXIDIZER OR FUEL RESERVOIR
T_2 TEMPERATURE CONTROLLER, TEST FIXTURE
P_1 & P_2 VALVES FOR CONTROLLING RESERVOIR PRESSURE

S_1 RESERVOIR HEATER S_4 SOLENOID VALVE
S_2 CYLINDER HEATER S_5 CYCLE TIMER
S_3 BLOWER S_6 STRAIN GAUGE ASSEMBLY

Figure 2 - Thiokol-RMD Dynamic O-ring Tester

TABLE VI

RESULTS OF THIOKOL-RMD DYNAMIC O-RING TEST
IN MIXED HYDRAZINE FUELS, 10,000 CYCLES

Formulation No.	Fuel	Temperature, °F	Pressure, psig	Appearance After Test
33	50/50 N_2H_4/UDMH	RT	atm	No wear
	50/50 N_2H_4/UDMH	160	500	Excessive surface wear
34	50/50 N_2H_4/UDMH	RT	1000	Slight wear, tack, no leaks
	50/50 N_2H_4/UDMH	160	1000	Slight wear, no leaks
	MMH	-60	1000	Leakage after 4500 cycles, O-ring twisted, wear after 10,000 cycles
35	50/50 N_2H_4/UDMH	RT	1000	No wear, no leaks
	50/50 N_2H_4/UDMH	160	1000	No wear, no leaks
	MMH	-60	1000	No wear, no leaks
	MMH	160	1000	No wear, no leaks

90

TABLE VII

COMPATIBILITY OF ELASTOMERS IN N_2O_4 AT ROOM TEMPERATURE

Formulation No.	Elastomer Vulcanizates	Volume Swell, % Days Immersed		Retention of Physical Properties
		1	7	
Silastic LS53	Silicone	280	385	Good
Silastic LR422	Silicone	273	290	Good
75-85	Viton B	284-410	280-525	Poor to Excellent
94-99	Viton A	180-300	200-325	Poor to Good
98	Fluorel	273	295	Poor
--	TFNMTEE(1)	45	174	Poor
24-27	Hydropol	19	19	Degraded
39	Cured Polyethylene	19	19	No apparent change
41-47	Butyl	50	50	Reversion(2)
121	Butyl	--	30(3)	Fair
132	EPR	19	19	Very good up to 4 days

(1) Trifluoronitrosomethane-tetrafluoroethylene

(2) Degree of reversion depends upon cure system

(3) After 4 weeks - 33%, Fair property retention

apparently functioned as a lubricant in this dynamic test and reduced the O-ring wear. Composition 35 was superior to 34 in hydrazine-UDMH mixtures and in MMH. Figure 3 shows the O-rings after 10,000 cycles in 50/50 hydrazine/UDMH at 160°F. The "before and after" O-rings prepared from composition 35 were identical showing no evidence of wear due to the dynamic testing in the fuel.

Compatibility with Nitrogen Tetroxide (N_2O_4)

When this investigation was initiated in May, 1960, fluorocarbon elastomers such as Viton and fluorosilicone elastomer Silastic LS-53 were recommended for N_2O_4 application (2, 5). Silastic LS-53 was reported to swell approximately 40 % in N_2O_4." During a recheck of these data it was noticed that the Silastic LS-53 while still in the immersion tube was swollen several hundred percent. Similarly, Viton vulcanizates also exhibited several hundred percent swell in N_2O_4. This should be of little surprise since the polar polymers Viton and LS-53 were specifically designed for resistance to non-polar hydrocarbons. In an analogous fashion one would expect the non-polar polymers to exhibit relatively low volume changes in the polar N_2O_4 liquid. Table VII illustrates this point, the polar polymers such as the fluorosilicones, Vitons and Fluorel exhibit volume changes of approximately 300 percent whereas the hydrocarbon polymers such as polyethylene, butyl and ethylene-propylene rubber show volume changes below 50 percent.

The high volume swell of Viton and fluorosilicone elastomer in N_2O_4 can be rationalized on the basis of solubility parameters. Calculation of the solubility parameter of N_2O_4 is not straight-forward due to the dissociation of N_2O_4 to NO_2. Assuming a dissociation of approximately 16% at the boiling point and subtracting the heat of dissociation from the experimental heat of vaporization (4), the solubility parameter calculates to be 10.5. The solubility parameters for Viton and Silastic LS-53 are 9.3 (3) and 9.6 respectively as compared to 7.8 for Butyl rubber. It could therefore be predicted that the former two elastomers would exhibit a higher volume swell than the Butyl rubber.

The low volume swell reported in the literature for LS-53 is obviously due to the loss of nitrogen tetroxide (b. p. 70.1°F) during the measurement. During this investigation, linear change measurements were made while the specimen was still immersed in the test liquid and, in accordance with ASTM 1460-60, linear changes were related to volume swell. Figures 4 and 5 illustrate this method.

Green
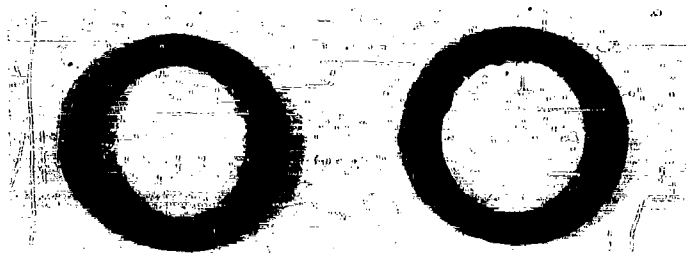
Compound 33

Compound 34
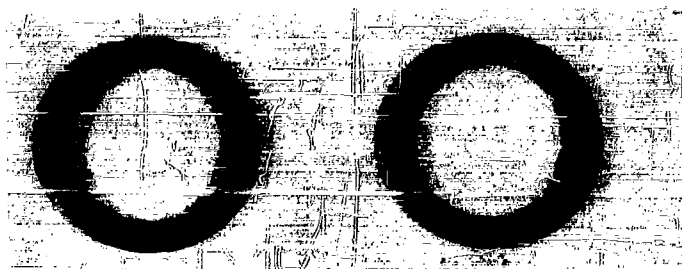
Compound 35

Figure 3 O-rings Cycled 10,000 Times at 160°F in 50-50
Mixture UDMH-Hydrazine, Pressurized to 500 psig
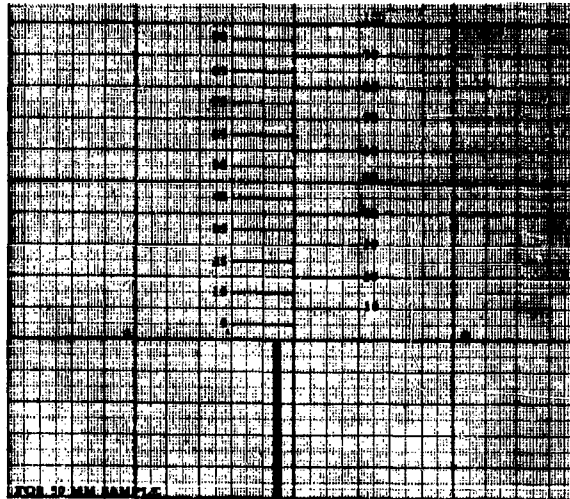
Figure 4   Linear Swell of LS-53, Seven Weeks
N_2O_4 (25 mm equals 238% volume swell)
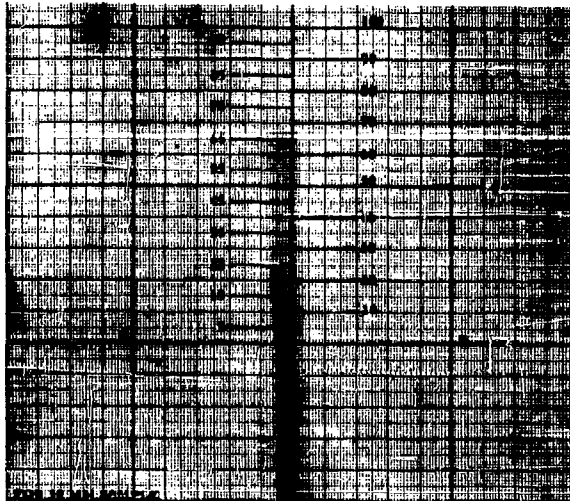
Figure 5   Silastic LS-53 One Hour After
Removal from N_2O_4

Measurement of the rate of swell of LS-53 in N_2O_4 showed that most of the swelling occurred in the first hour and a volume swell of approximately 300% was obtained after 24 hours of immersion (Figure 6). In performing this test it was noted that $N_2O_4 \rightleftharpoons NO_2$ began to diffuse from the swollen specimen, with concomitant shrinkage, immediately after its removal from the test liquid. After ten minutes the sample recovered to a total swell of 26% and after one hour it exhibited a swell of only 6% (Figure 7). This would account for the discrepancies in volume swell data reported in the literature and indicates that ASTM 1460-60 yielded the more reliable swelling data. After allowing the swollen specimens to return to their original dimensions they evidenced no significant loss in strength or elasticity (Table VII) as measured qualitatively.

It was noted that hydrocarbon polymers swell considerably less in liquid N_2O_4 than the fluorinated elastomers. It was also found that unsaturated polymers such as Hydropol degrade readily in N_2O_4 due to the addition of N_2O_4 to the double bond (Table VII). Polyethylene and polypropylene were immersed in N_2O_4 for seven days at room temperature and no apparent change was noted. However, neither polymer is sufficinetly elastomeric to be considered for many applications requiring elasticity. With this in mind, efforts were concentrated on non-polar polymers with little or no unsaturation, for example, butyl rubber and ethylene-propylene rubber.

Butyl rubber was formulated using three different curing systems, sulfur, GMF-red lead, and phenolic resin. The vulcanizates containing the first two curatives reverted during N_2O_4 immersion while the latter vulcanizate qualitatively showed a fair retention of physical properties. The effect of the degree of unsaturation was studied by evaluating various grades of butyl rubber and no significant differences in compatibility were obtained.

Residual unsaturation in the butyl vulcanizates would be expected to react with N_2O_4. In an effort to completely saturate the butyl rubber, the effect of increasing the phenolic resin curative on the N_2O_4 compatibility was evaluated. A qualitative evaluation showed that the vulcanizates which contained the higher percentages of phenolic resin retained more strength after immersion.

Ethylene-propylene rubbers (EPR) are saturated hydrocarbon copolymers which can be crosslinked with organic peroxides. Ethylene-propylene terpolymers containing unsaturation by incorporating various unsaturated monomers are also becoming
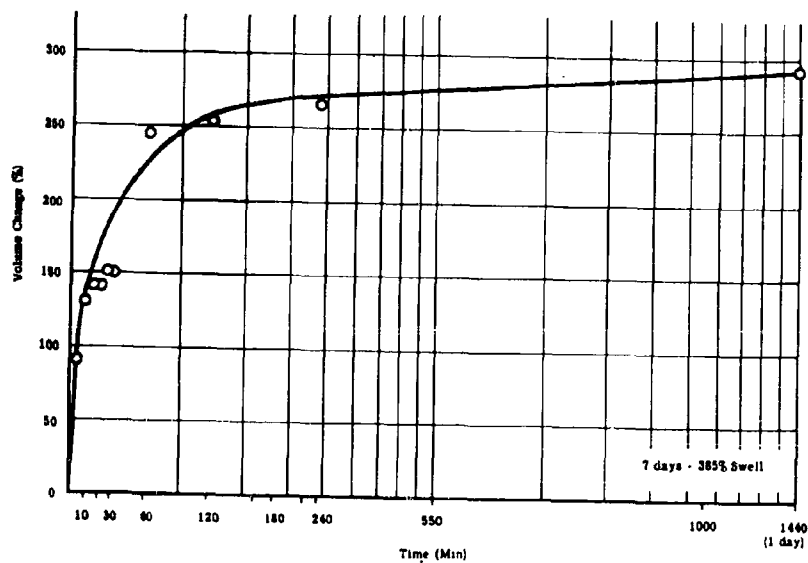
Figure 6   Swell of Silastic LS-53 in N_2O_4
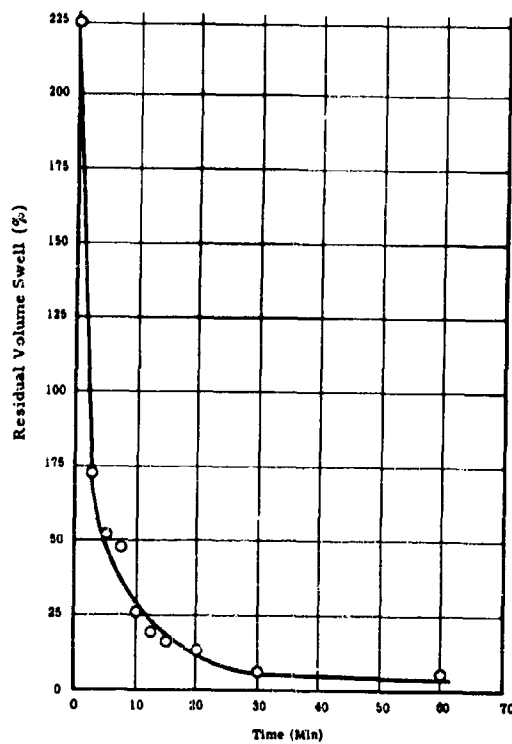
Figure 7   Recovery of Silastic LS-53 after Removal From N_2O_4

available. Initial qualitative compatibility studies with the copolymer showed the EPR vulcanizates to be compatible with N_2O_4 for short periods of time. They exhibited a volume swell of only 19% as compared to approximately 30% for the best butyl rubber compositions.

An exhaustive screening of many butyl and EPR formulations for compatibility with N_2O_4 revealed several factors which warranted closer investigation. With this in mind, several of the more promising compositions were evaluated quantitatively. Table VIII lists these formulations. Immersion data were obtained at $60^{\circ}F$ and $70^{\circ}F$ for up to seven days immersion and the data are summarized in Tables IX, X, and XI. Micro-dumbbell tensile specimens, 2 inches long with a necked down area 1/8 x 5/8 inch were used. These specimens were outgassed before testing by a three step process: (1) 4 hour suspension in air at ambient temperature and pressure, (2) 24 hour vacuum treatment at room temperature, (3) 24 hour rest period at ambient conditions.

Butyl composition 121 shows excellent retention of its physical properties after seven days immersion in N_2O_4 at $60^{\circ}F$ (Figure 8). However, at $70^{\circ}F$ the mechanical properties appear to drop off rapidly after one day immersion, and then remain approximately constant for the following six days of immersion (Figure 9). The final properties are sufficiently high, however, to consider this composition for application studies (Table IX). Discrepancies in the ultimate elongation were observed for different mill batches, and may be attributed to variations in the processing or curing temperature. This may have also had an effect on the immersion results. Volume swell for compound 121 is also affected by temperature and is somewhat higher at $70^{\circ}F$ compared with that obtained at $60^{\circ}F$ (Table XI and Figure 10).

The three ethylene-propylene formulations which were evaluated quantitatively contained carbon black (formulation 132), magnesium oxide (formulation 180) or a mixture of the two (formulation 197) as fillers. Composition 180 and 197 retained a large portion of their original properties after seven days immersion at $60^{\circ}F$. Composition 132 appears to be promising for applications up to five days at $60^{\circ}F$ (Figure 8). At $70^{\circ}F$, however, all the compositions have either degraded or swollen excessively after five days immersion (Tables X, XI, and Figure 9). The presence of such a critical temperature would appear to be due to greater dissociation of the N_2O_4 to NO_2 at the higher temperature. Compatibility data obtained by immersing the samples in sealed tubes of N_2O_4 to

TABLE VIII

FORMULATIONS OF PROMISING COMPOSITION FOR N_2O_4 APPLICATION

Formulation No.	121	192	132	180	197
Butyl 218	100	---	---	---	---
Butyl 325	---	100	---	---	---
EPR 404	---	---	100	100	100
Statex R (HAF)	65	65	50	---	25
Magnesium Oxide	---	---	---	50	25
ZnO	5	5	---	---	---
Amberol ST-137	50	50	---	---	---
Hypalon 20	5	5	---	---	---
DiCup 40C	---	---	10	10	10

TABLE IX

EFFECT OF N_2O_4 IMMERSION ON PROPERTIES

OF BUTYL COMPOSITION

Formulation No.	121	121
Immersion Temp., °F	$60° \pm 1°$	$70° \pm 2°$
Original Properties (1,2)		
200% Modulus, psi	1850	1830
Tensile Strength, psi	1850	2020
Elongation, %	200	225
Shore A Hardness	90	90
Aged 1 Day in N_2O_4 [3]		
200% Modulus, psi	1610	1540
Tensile Strength, psi	1880	1640
Elongation, %	275	225
Aged 3 Days in N_2O_4 [3]		
200% Modulus, psi	1450	1440
Tensile Strength, psi	1710	1560
Elongation, %	250	250
Aged 5 Days in N_2O_4 [3]		
200% Modulus, psi	1320	1350
Tensile Strength, psi	1680	1550
Elongation, %	300	275
Aged 7 Days in N_2O_4 [3]		
200% Modulus, psi	1610	1320
Tensile Strength, psi	1730	1490
Elongation, %	275	250

----

(1) Median of 5 results
(2) Specification after seven days immersion

        Tensile Strength, psi   500 min
        Elongation, %   100-600
        Shore A Hardness   40-90

(3) Properties obtained after outgassing

TABLE X

EFFECT OF N_2O_4 IMMERSION ON PROPERTIES OF ETHYLENE/PROPYLENE RUBBER COMPOSITIONS

	#132		#180		#197	
Original Properties						
200% Modulus, psi	740		220		420	
Tensile Strength, psi	2000		510		1720	
Elongation, %	350		475		450	
Shore A, points	62		35		59	
Immersion Temp, °F	60°±1°	70°±2°	60°±1°	70°±2°	60°±1°	70°±2°
Aged 1 Day in N_2O_4						
200% Modulus, psi	450	230	530	600	670	660
Tensile Strength, psi	1580	830	700	660	1460	1160
Elongation, %	550	700	450	425	500	525
Shore A, points	59	53	59	69	62	67
Aged 3 Days in N_2O_4						
200% Modulus, psi	300	36	710	610	730	610
Tensile Strength, psi	1070	38	780	610	1350	740
Elongation, %	700	225	400	200	525	500
Shore A, points	55	15	66	61	67	68
Aged 5 Days in N_2O_4						
200% Modulus, psi	150	(1)	530	(1)	510	---
Tensile Strength, psi	520		620		1060	155
Elongation, %	800		500		600	150
Shore A, points	64		66		65	21
Aged 7 Days in N_2O_4						
200% Modulus, psi	110	(1)	680	(1)	670	(1)
Tensile Strength, psi	230		700		940	
Elongation, %	950		400		500	
Shore A, points	37		64		63	

(1) Degraded or severely swollen

TABLE XI

EFFECT OF N_2O_4 IMMERSION ON VOLUME CHANGE [1,5]

% Volume Swell [2]

Formulation No.	121		132		180		197	
Immersion Temp, °F	60±1°	70±2°	60±1°	70±2°	60±1°	70±2°	60±1°	70±2°
Days Aging in N_2O_4								
1	16	(3)	9	30	48	82	26	52
3	20	(3)	13	30	60	100	30	56
5	23	(3)	13	23	77	130	41	100
7	26	30	16	(4)	91	(4)	56	(4)

(1) ASTM D 1460-60
(2) Average of two results
(3) No data available
(4) Degraded after 5 days in N_2O_4 at 70±2°F
(5) Specification after seven day immersion
    Volume Swell - 30% Max
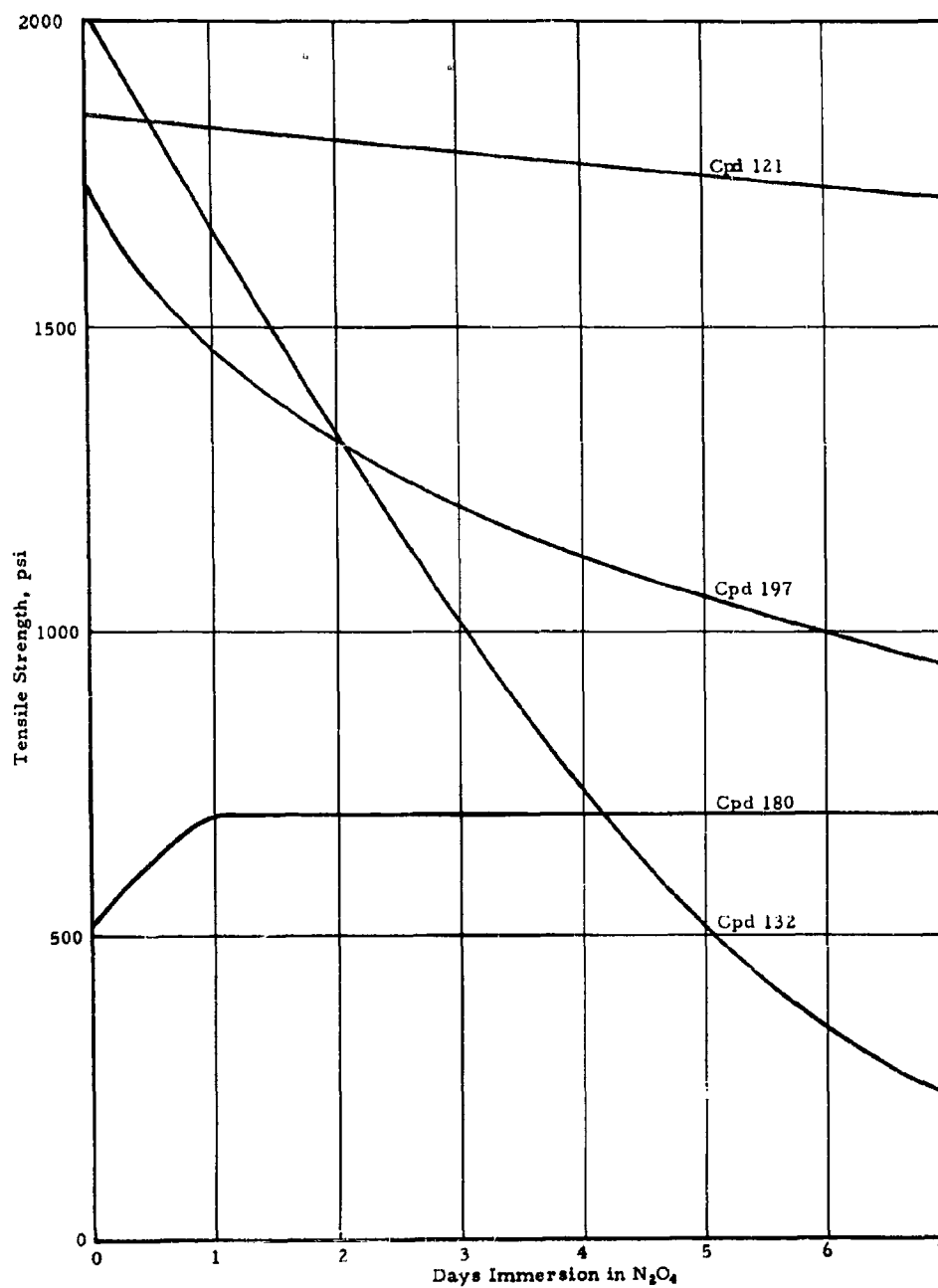
Figure 8 Effect of N_2O_4 Immersion at $60 \pm 1^{\circ}F$ on Tensile Strength After Outgassing
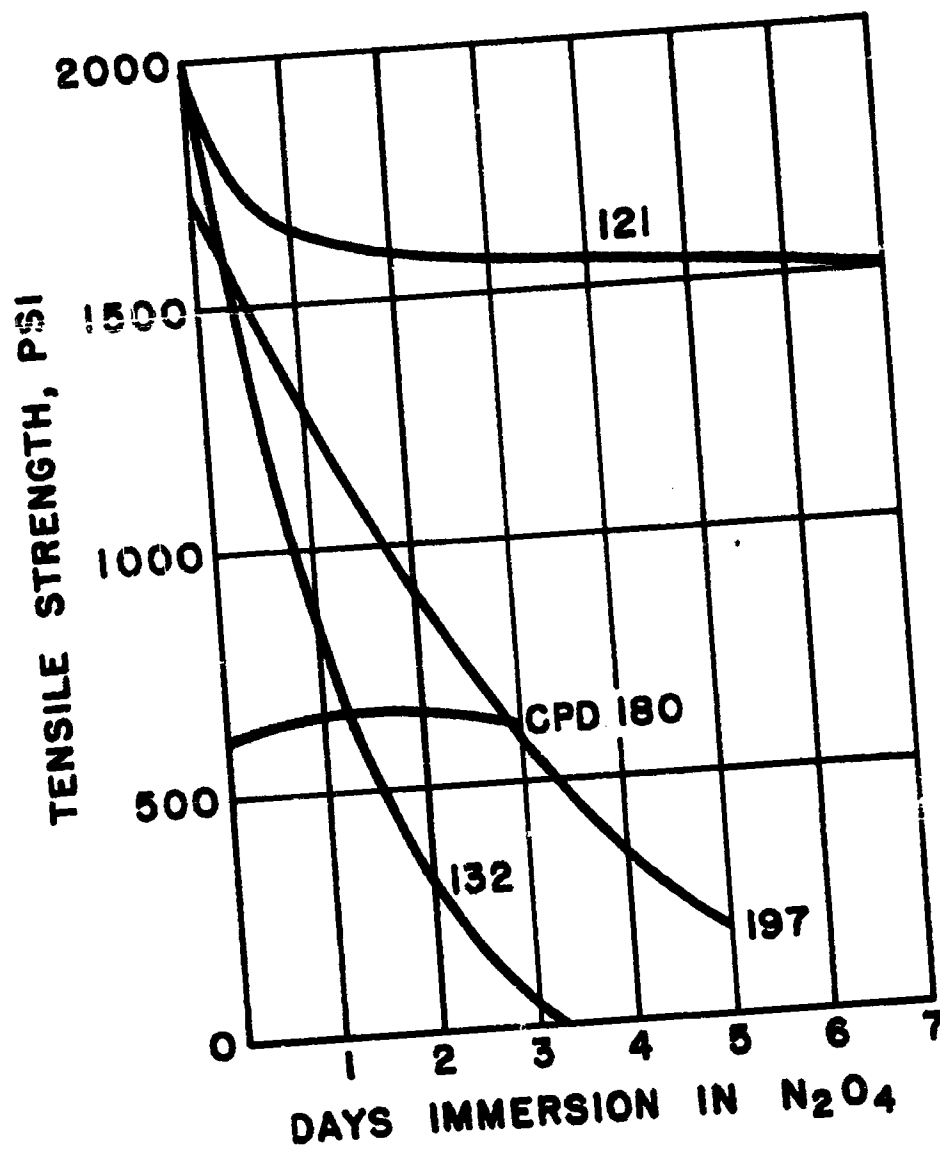
Figure 9 Effect of N_2O_4 Immersion at $70 \pm 2°F$ on Tensile Strength after Outgassing

depress the dissociation, showed no substantial improvement in compatibility.

Table X shows that EPR compositions containing magnesium oxide (formulation 180) as the filler retain a greater portion of their physical properties than the carbon black filled compositions. The mixed filler (formulation 197) had intermediate physical properties after immersion. Qualitative data indicate that other metal oxides also show this increase in compatibility. The volume swell data, however, show excessive swelling of the magnesium oxide filled vulcanizates (Table XII). The effect of N_2O_4 immersion on tensile strength and volume swell is shown graphically in Figures 8, 9 and 10.

Ethylene-propylene copolymers of 95/5 and 90/10 ethylene/propylene composition were evaluated for compatibility in N_2O_4. After five days immersion at $60^{\circ}F$ only a small change in physical properties was obtained (Table XII). These compositions differ from the previous ones in both monomer ratio and in filler content.

EPR composition 132 was evaluated in a mixture of 90/10 N_2O_4/NO at $100^{\circ}F$ for 4 hours. The high freezing point of N_2O_4 ($12^{\circ}F$) necessitates the addition of NO to lower the freezing point for many applications. The results are tabulated in Table XIII and show composition 132 to be compatible for this period of time.

O-rings were prepared from the most promising materials and tested in the Thiokol - RMD dynamic O-ring tester at room temperature and $160^{\circ}F$ while in contact with liquid N_2O_4 at 250 psig (Table XIV). The best results were achieved with peroxide cross-linked polyethylene (formulation 39). These O-rings lasted 10,000 cycles at $160^{\circ}F$ with no sign of liquid N_2O_4 leakage. The second best material and the best elastomer was EPR. Although no leakage of liquid N_2O_4 was obtained after 10,000 cycles at room temperature, one of the O-rings broke at 3788 cycles when tested at $160^{\circ}F$. This specimen appears to be good otherwise, and the rupture may have been due to faulty molding. Figures 11 and 12 show these O-rings after the dynamic test. The butyl composition containing large quantities of phenolic resin (formulation 121) withstood 7100 cycles at room temperature before a liquid leak developed. These O-rings showed some wear, possibly due to the stiffness of the compound (Figure 13).

TABLE XII

EFFECT OF N_2O_4 IMMERSION ON EXPERIMENTAL ETHYLENE-PROPYLENE COPOLYMERS

Formulation No.	A103	A104	A105	A106
K-11041 Resin	---	---	100	100
K-11042 Resin	100	100	---	---
Dicumyl Peroxide	4	---	---	4
C_2/C_3 Ratio	95/5	95/5	90/10	90/10
Original Properties				
200% Modulus, psi	1500	1570	1830	---
Tensile Strength, psi	1610	2540	3000	1700
Elongation, %	300	600	650	75
Shore A, Points	93	97	96	98
Aged in N_2O_4, 5 days $60 \pm 1°F$				
200% Modulus, psi	---	1580	1830	---
Tensile Strength, psi	1390	1890	2810	1570
Elongation, %	175	600	600	100
Shore A, Points	95	96	97	95
Volume Change, %	6	9	13	16
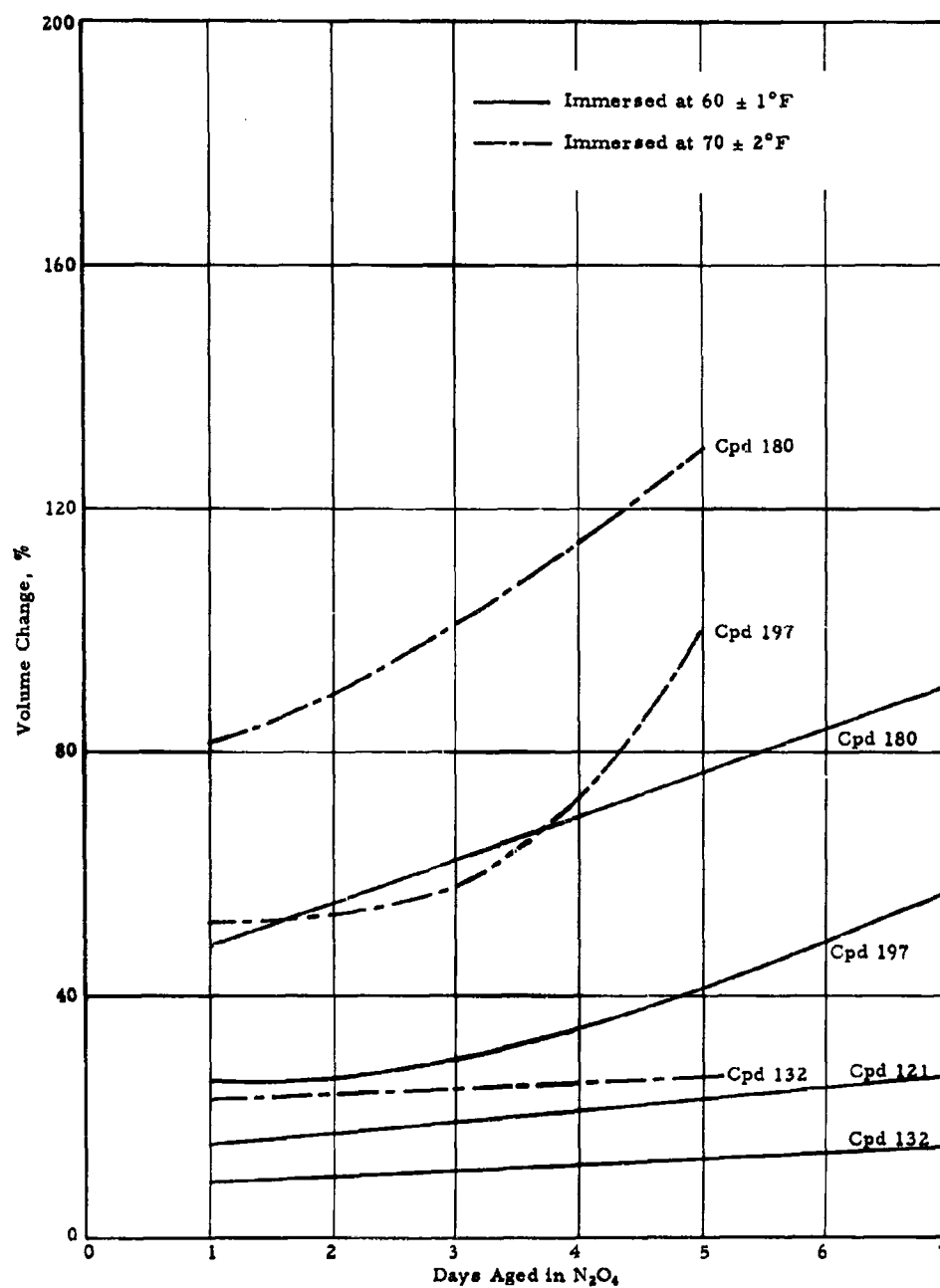
Figure 10 Effect of N_2O_4 Immersion on Volume Swell

TABLE XIII

FORMULATION 132 AFTER 4 HOURS AT 100°F
IN 90/10 N_2O_4/NO

	Original	After Immersion
Tensile Strength, psi	2000	1050
Elongation, %	375	750
Shore A	---	60
ΔL, %	---	11
ΔV, %	---	36

TABLE XIV

DYNAMIC TEST RESULTS OF PROMISING MATERIALS FOR N_2O_4 APPLICATION[1]

Base Polymer	Temp °F	Liq. Leak, Cycles	Test Terminated	Chg. in Shore A	Appearance and Remarks
PE[2] 39-1	160	-	10,000	±0	Wear, no leak
PE -2	160	-	10,000	±0	Wear, no leak
Butyl 44-1	160	early in test	10,000	-35	Leakage, O-ring distorted
Butyl -2	160	early in test	10,000	-35	Leakage, O-ring distorted
Butyl 121-1	R. T.	-	7,100	-40	Considerable wear
Butyl -2	R. T.	7,100	7,100	-40	Wear - stretched
Butyl -3	160	1,000	1,000	-30	Failed due to wear
Butyl -4	160	1,000	1,000	-30	Failed due to wear
EPR 132-1	R. T.	-	10,000	-15	Slight wear
EPR -2	R. T.	-	10,000	-15	Slight wear
EPR -3	160	3,788	3,788	-20	Ring broke, faulty molding
EPR -4	160	-	3,788	-20	Slight wear

(1) at 250 psig

(2) polyethylene

Figure 11 EPR O-rings after 10,000 Cycles in Thiokol-
RMD Tester with N_2O_4 at Room Temperature
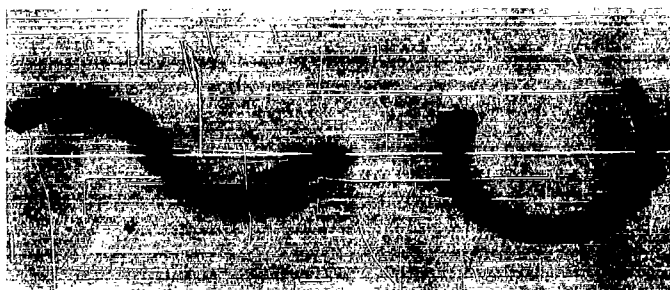
Figure 12 EPR O-rings after 3788 Cycles in Thiokol-RMD
Tester at 160°F (Ring on left failed and other was cut)

Figure 13 Butyl O-rings (formulation 121) after 7100 Cycles
in Thiokol-RMD Tester at Room Temperature

Fluorine Containing Oxidizers

Many of the fluorine containing oxidizers are gases at room temperature and are characterized by their reactivity with metals, organic materials and moisture. The oxidizers of current interest are perchloryl fluoride (ClO_3F), nitrogen tetrafluoride (N_2F_4) and chlorine trifluoride (ClF_3). Because of the high vapor pressure and low critical temperature of N_2F_4, various mixtures are also of interest.

Compatibility testing in fluorine-containing oxidizers is accomplished by using a metal vacuum rack. The use of the vacuum rack results in a safe and rapid evaluation. Transparent Kel-F tubes machined from solid rods and pressure tested with nitrogen up to 1000 psi are used. They are connected to a valve so that they can be removed from the rack for long term conditions (Figure 14).

The evaluation procedure consisted of washing the cured specimens (2 mm x 2 mm x 10 mm) with CCl_4, mounting them on the rack in the Kel-F tubes and vacuum treating them for at least two hours. The tube and specimen were then cooled in liquid nitrogen and enough oxidizer was introduced to completely cover the specimen. The liquid nitrogen cooling bath was then removed, and the specimen brought to room temperature and allowed to remain under ambient temperature conditions for the duration of the immersion period. Swelling measurements and observations were made at regular intervals. Following the immersion period, the oxidizer was pumped from the tube and the specimen subjected to vacuum for about one hour before removal from the tube for physical examination.

Perchloryl Fluoride

The most promising materials found as a result of screening tests in ClO_3F were evaluated further at room temperature for one and seven days immersion (Tables XV and XVI). The fluorinated elastomers exhibited swelling in ClO_3F. SBR embrittled after seven days exposure indicating either crosslinking or degradation due to reaction with ClO_3F. Silastic LS-53 retained a 24 percent volume swell after 48 hours immersion at $-180°F$ and subsequent vacuum treatment for thirty minutes. The EPR showed a swell of only 13% after seven days immersion at ambient temperature with no apparent change in physical properties. After vacuum treatment, the elastomer showed a 6% volume shrinkage. The EPR was further characterized by evaluating the strength

110
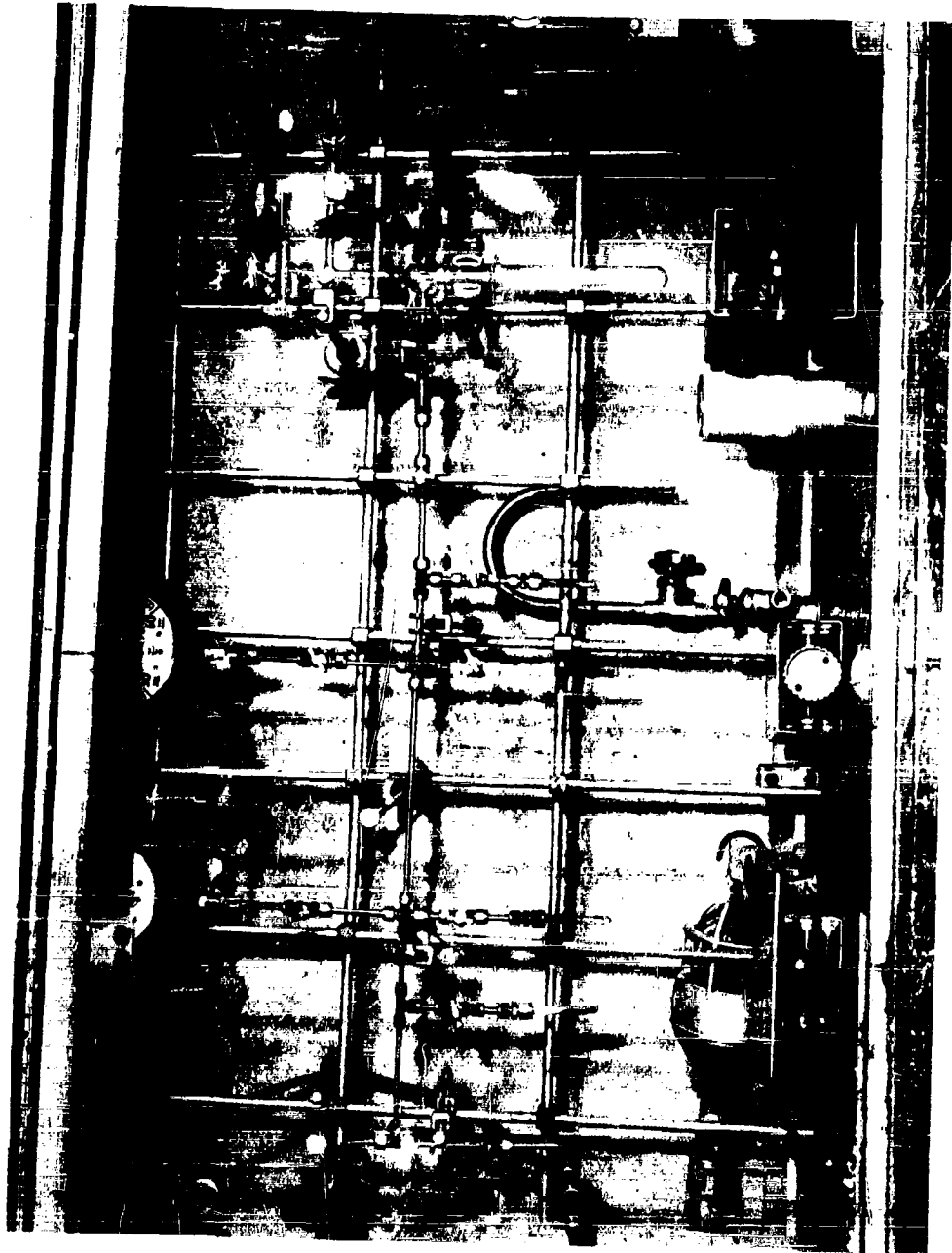
Figure 14 - Vacuum Rack for Polymer Evaluation in Fluorinated Oxidizer

Green

TABLE XV

FORMULATIONS OF COMMERCIALLY AVAILABLE ELASTOMERS FOR COMPATIBILITY WITH ClO_3F AND N_2F_4

Formulation No.	36	132	161	162	LS-53
Viton B	100	--	--	--	--
EPR	--	100	--	--	--
Synpol 1551	--	--	100	--	--
Kel-F 5500	--	--	--	100	--
Magnesium Oxide	15	--	--	--	--
Thermax (MT)	20	--	--	--	--
Diak No. 1	3	--	--	3	--
Kosmos 60	--	50	--	--	--
DiCup 40C	--	10	--	--	--
Cab-O-Sil	--	--	25	--	--
Stearic Acid	--	--	2	--	--
Zinc Oxide	--	--	5	10	--
Sulfur	--	--	2	--	--
Altax	--	--	1	--	--
Unads	--	--	0.5	--	--
Dyphos	--	--	--	10	--
Cure - Time (min)/Temp (°F)	30/300	40/320	30/290	30/350	--
Post Cure - Time (hr)/Temp (°F)	24/400	--	--	16/350	--

Green

TABLE XVI

COMPATIBILITY OF COMMERCIALLY AVAILABLE ELASTOMERS IN ClO_3F

Vulcanizate No.	36	162	132	161	LS-53[1]
Rubber Base	Viton-B	Kel-F 5500	EPR	SBR (Cold)	Fluorosilicone
1 Day Immersion at R.T.					
Volume Swell, %	73	ca 200	16	0	[2]
7 Day Immersion at R.T.					
Volume Swell, %	73	--	13	ca 30	
Appearance	Good	Blistered	Good	Good	Good
Retention of Strength	Good	Good	Good	Embrittled	Good
Retention of Elasticity	Good	Good	Good	Embrittled	Good

(1) Immersion time 48 hours at -100°F

(2) After vacuum treatment, retained 24% swell

113

retention of micro-dumbbell specimens after one and seven days in ClO_3F at ambient temperature. Upon completion of the immersion period, the ClO_3F was vented and each specimen was subjected to vacuum conditions for about one hour before removal for physical testing. Tensile strength, ultimate elongation and modulus at 200% elongation was obtained using ASTM standard techniques. The results show a decrease in tensile strength and modulus accompanied by an increase in elongation (Table XVII). Assuming that all the ClO_3F had been removed as a result of the vacuum treatment, the data are indicative of a decrease in crosslink density.

Nitrogen Tetrafluoride (N_2F_4)

A literature search for elastomers compatible with N_2F_4 yielded little information. The only compliant polymeric materials mentioned as having been used without series difficulty in gaseous service are Teflon, Kel-F, polyethylene and Tygon (6). Since an important future consideration is the use of N_2F_4/ClO_3F mixtures, it was decided to evaluate the same materials which were evaluated in ClO_3F. The specimens were immersed at -100^0F (approximate boiling point of N_2F_4) for 48 hours using the vacuum rack technique. No indication of any change in appearance, strength, elasticity, or volume was observed for any of the materials.

EPR, formulation 132, was evaluated in N_2F_4 and in ClO_3F/N_2F_4 (50/50 by volume). Once again the vacuum rack method was used. Physical properties were obtained using ASTM standard techniques.

The results of the 50/50 ClO_3F/N_2F_4 evaluation are summarized in Table XVIII and indicate that the EPR (132) is satisfactory for this application. Compatibility testing in 100 % N_2F_4 at room temperature was unsuccessful; after two hours the Kel-F immersion tubes exhibited what appeared to be cold flow ruptured due to the high vapor pressure of the N_2F_4 (>400 psi). No degradation of the elastomer due to the oxidizer was noted during this limited immersion time.

Chlorine Trifluoride (ClF_3)

Early efforts demonstrated that very few organic materials were compatible with chlorine trifluoride. The fluorocarbons appeared to be the only polymers with a chance of being used in contact with ClF_3 and therefore, a screening study was conducted with the various fluoropolymers using the vacuum rack technique

TABLE XVII

PHYSICAL PROPERTIES OF EPR FORMULATION 132
AFTER IMMERSION IN ClO_3F AT AMBIENT ROOM TEMPERATURES

Immersion Time, Days	Tensile Strength, psi	Elongation, %	200% Modulus, psi	Volume Swell, %
Original	1965	415	420	-
1	1375	470	330	-
7	1000	550	260	13

TABLE XVIII

PHYSICAL PROPERTIES OF EPR FORMULATION 132
AFTER IMMERSION IN 50/50 ClO_3F/N_2F_4 AT ROOM TEMPERATURE

	Original	After 10 Days Immersion
Tensile, psi	1970	1370
Elongation, %	415	425
200% Modulus, psi	420	500
Volume Swell, %	-	0[1]

(1) ASTM D 1460-60- 4 days immersion

described. The polymers shown in Table XIX were immersed in ClF_3 for five days at ambient room temperature.

Trifluoronitrosomethane-tetrafluoroethylene (TFNMTFE) raw gum seemed to have a refractive index quite similar to the ClF_3 which rendered it almost invisible, and therefore, difficult to obtain swell measurements. However, it did not noticeably swell or react during the 5 day immersion period. Examination of the specimen after removal from the tube showed no volume change or sign of degradation. Immersion of amine cured TFNMTFE in ClF_3 resulted in moderate bubbling as soon as the ClF_3 liquefied. The reaction continued for about 1 hour and the specimen appeared degraded. After five days it was removed from the tube and found to have become soft and gummy. It had also lost its original brownish color and became milky and translucent. Silica rein-forced - amine cured TFNMTFE began bubbling fairly vigorously as soon as the ClF_3 liquefied and continued for about one hour. After 5 days it was removed and found to be soft, gummy and translucent. Before the test it had been opaque.

To summarize these results, the base TFNMTFE elas-tomer gum appears unaffected by liquid ClF_3 at room temperature. The crosslinks and the silica filler are apparently attacked by the oxidizer leaving the specimens softer than the original raw gum after immersion. The bubbling action combined with the disap-pearance of the opaque nature of the filled polymer indicates that the SiO_2 filler was converted to SiF_4 gas.

Specimens of Viton A, B, Kel-F5500, and Fluorel gums were evaluated in ClF_3 for 5 days at room temperature using the vacuum rack technique. The Viton A and Fluorel gums were softened by the ClF_3 and although there did not appear to be any chemical reaction both materials flowed to the bottom of the tube. They were still rubbery, however, after five days immersion. The Kel-F 5500 did not seem to react with the ClF_3 vapors but when the liquid was introduced, the polymer ignited and burned vigorously. The tube containing the Viton B developed a leak allowing the ClF_3 to escape within approximately 2 hours. The gum was unaffected by this short exposure.

Perfluoroamidine elastomer did not appear to be affected by ClF_3, but when a trace of grease was present the elastomer burned very rapidly.

TABLE XIX

EVALUATION OF VARIOUS POLYMERS IN ClF$_3$

Polymer	Remarks
TFNMTFE (Gum)	No sign of reaction, no change in specimen after 5 days at room temperature.
TFNMTFE[1]	Reacted immediately, degraded after 5 days, lost original brownish color, became milky, translucent, and gummy.
TFNMTFE[2]	More vigorous reaction otherwise same as above.
"H"-Film[3]	Dissolved, probably reacted within a few minutes.
Perfluoroamidine Elastomer[3]	Did not seem to react but continued to burn in ClF$_3$ when ignited.
Viton A Gum	No sign of reaction, softened and flowed to bottom of tube.
Viton B Gum	Unaffected in 2 hours exposure.
Fluorel Gum	Same as Viton A.
Kel-F 5500 Gum	Burned vigorously.

----

(1) TFNMTFE gum - 100 g; triethylene tetramine - 1.56 g; cured 60 min at 212°F; Post cured 18 hr at 212°F.

(2) Same as (1) plus Hi-Sil X303 - 15 g.

(3) Subjected only to screening test.

117

A series of Viton compounds was prepared using the formulations listed in Table XX. The samples marked A and B were not cured. Specimens of these materials were exposed to ClF_3 vapors and no reaction was noticed. Compositions A, B, and 165 dissolved within 1-2 hours and the others all swelled to approximately twice their original length (ΔL equivalent to over 700 percent volume swell). After 24 hours, formulation 168 had apparently dissolved while the others were swollen three or four times their original size. One specimen of formulation 169 vulcanizate was removed after 24 hours immersion and found to have retained a fair amount of strength. The remaining two compounds, as well as a second sample of 169, had swelled to five or six times their original size after seven days immersion and crumbled when vented to the atmosphere.

TFNMTFE was the most promising elastomer of all those screened. The base gum appeared unaffected by liquid ClF_3 after five days exposure at room temperature. The only available vulcanizate of this elastomer (triethylenetetramine curative, silica filled) degraded upon immersion; both the crosslinks and the silica were attacked by the oxidizer leaving the specimens softer than the original raw gum after immersion. The sample did not retain its configuration but flowed to the bottom of the tube. A curing study of TFNMTFE was therefore initiated. To accomplish as much as possible with a limited amount of material, micro-compounding techniques were employed. Five gram samples of the gum were mixed on a 1" x 4" rubber mill and cured in 1/2" x 2 1/2" strips. Specimens were prepared using a micro-dumbbell die with a length of 1", width of 1/4" at the wide portion, and a "necked down" portion of 3/16".

Triethylenetetramine and a combination of triethylenetetramine and hexmethylenediamine carbamate are the only successful curing systems reported for the TFNMTFE. In an effort to develop a crosslinking system which would be compatible with ClF_3 other basic catalysts such as aromatic amines, (imidazole, pyrazine, piperazine) and the sodium salt of hydroquinone were evaluated as curatives. None of the amines appeared to cure the rubber satisfactorily although the imidazole containing samples was more resilient than the pure gum indicating a partial cure. The sodium salt of hydroquinone resulted in a cured elastomer. Evaluation of concentrations of 1 to 20 phr yielded vulcanizates which ranged in properties from soft, partially cured elastomers to resinous products. The cured products were aged seven days in ClF_3 at room temperature. Although they retained their configuration and some elasticity, they swelled

TABLE XX

VITON FORMULATIONS FOR EVALUATION IN ClF₃

Formulation No.	A	B	165	166	167	168	Green 169
Viton B	100	100	---	---	---	100	100
Viton A	---	---	100	100	100	---	---
Teflon FEP	25	---	---	---	---	---	---
Polyvinyl fluoride	---	25	---	---	---	---	---
Diak No. 1	---	---	1	1	1	1	1
Magnesium oxide	---	---	---	15	15	---	15
Acetylene Black	---	---	---	---	15	---	---
Thermax (MT)	---	---	---	---	---	---	15
Cure – Time (min)/Temp (°F)	---	---	30/300	30/300	30/300	30/300	30/300
Post Cure – Time (hr)/Temp (°F)	---	---	24/400	24/400	24/400	24/400	24/400

excessively.

Resin Coated Elastomers

Several compliant resins are more compatible with some of the more reactive rocket propellants than commercially available elastomers. A coating of such a resin on an elastomeric base may be sufficiently compliant to maintain the elastomeric properties of the base material and yet shield the elastomer from the propellant.

A polyethylene coated O-ring which maintains the elastic properties of the base elastomer is illustrated in Figure 15. The Microthene 608 coated O-ring can be elongated more than 50 %, twisted, and allowed to recover with no visible damage to the coating. In the photograph, this O-ring is compared to one which is coated with a low molecular weight polyethylene which cracked and flaked.

Various elastomers were used as base materials and coated with such resistant polymers as high and low density polyethylene, Kel-F, Teflon TFE and Teflon FEP. The coating techniques evaluated were the fluidized bed, disperson and emulsion dips, and a solution dip, all followed by sintering. The most promising coatings were evaluated by immersing the coated O-rings into liquid N_2O_4 at room temperature. In every case the O-rings either swelled or degraded in less than 24 hours even though the coating on the O-ring appeared to be continuous to the naked eye. When the coated O-rings were examined under a microscope, tiny bubbles and other imperfections were noted. It could not be determined with certainty whether the imperfections would expose the base O-ring to the immersion media, or whether the coated resins were sufficiently permeable to $N_2O_4 \rightleftharpoons 2NO_2$. It is obvious, however, that in order to achieve the requisite protection a permeability approaching zero is necessary for a low degree of swelling of the base elastomer.

Metal Coated Elastomers

Organic polymers are inherently unstable in strong oxidizers and therefore metal coatings on elastomeric O-rings were contemplated. Just as a resin coated elastomer maintains some of the elastic properties of the base material, an extremely thin metal coating could be expected to yield a flexible O-ring composite. In addition, a continuous metal coating would be expected to be impermeable to the propellants.

120
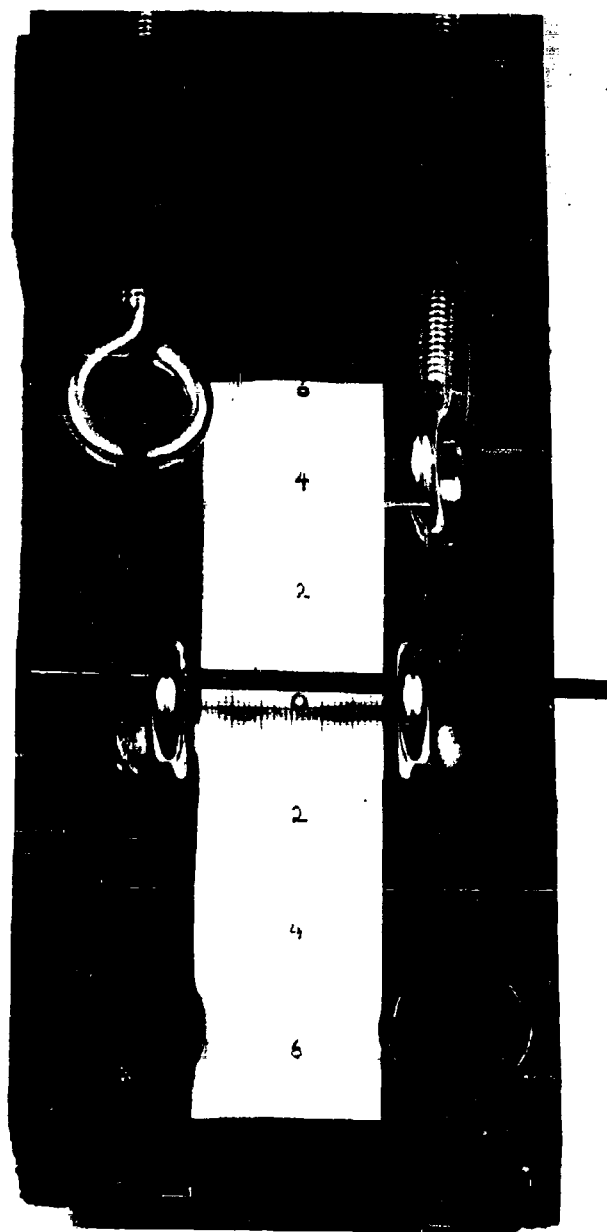
Figure 15   Stressed Polyethylene Coated O-rings
Left - Microthene 608
Right - AC 617A Polyethylene

The feasibility of this approach is illustrated by a butyl rubber -aluminum foil (1.5 to 2.0 mils thick) laminate, prepared by pressure molding with concomittant curing of the rubber. The result was a laminate with excellent adhesion of the metal to the rubber. It could be flexed repeatedly a full 180° to a sharp bend with the aluminum either in extension or compression without. cracking the aluminum. Gold foil-rubber laminates have also been prepared. The aluminum laminates were evaluated as gaskets for N_2O_4 in the apparatus shown in Figure 16. The test involves clamping a flat coated sheet of material against the lips of a glass tube which has been partially filled with liquid N_2O_4. The specimen is held firmly enough to effect a seal thereby preventing the N_2O_4 from escaping when the jib is inverted. After four weeks of exposure of the laminate with the aluminum side exposed to N_2O_4 at ambient room temperature there was not visible degradation to either the aluminum or the elastomer. No N_2O_4 was lost either through leakage or permeation, In a series of experiments, pin-holes were made in aluminum coating and the laminate was exposed to N_2O_4 for 72 hours. Figure 17 shows the aluminum blistered at the pinhole site. Immediately behind these pinhole sites the rubber showed swelling or bulging.

In addition to the lamination technique three methods of coating elastomers with metal films have been investigated, namely, vacuum deposition, chemical deposition, and electro-plating. The films obtained by the vacuum deposition technique rubbed off easily unless an overcoat of magnesium fluoride was vacuum deposited. The coatings obtained did not appear to be continuous. A gold coated elastomer observed under a microscope revealed the gold coating as many tiny platelets lying side by side on the elastomer surface.

The chemical deposition techniques investigated were 1) the utilization of gold and platinum complex solutions which decomposed upon heating 2) the reduction of a metal onto a surface previously treated with a reducing agent (e.g., formaldehyde) and 3) the replacement of a metal of lower electronegativity, previously deposited on the elastomer, by gold from solution. Gold and platinum complex solutions have been utilized for the deposition of gold and platinum protective coatings. They have also been investigated as conductive substrates for further electrodeposition. Little success has been achieved in either case. Several methods of depositing metals by chemical reduction have been investigated. The deposition of copper by the Shipley Copper Process resulted in a satisfactory appearing, conductive coating; this coating showed
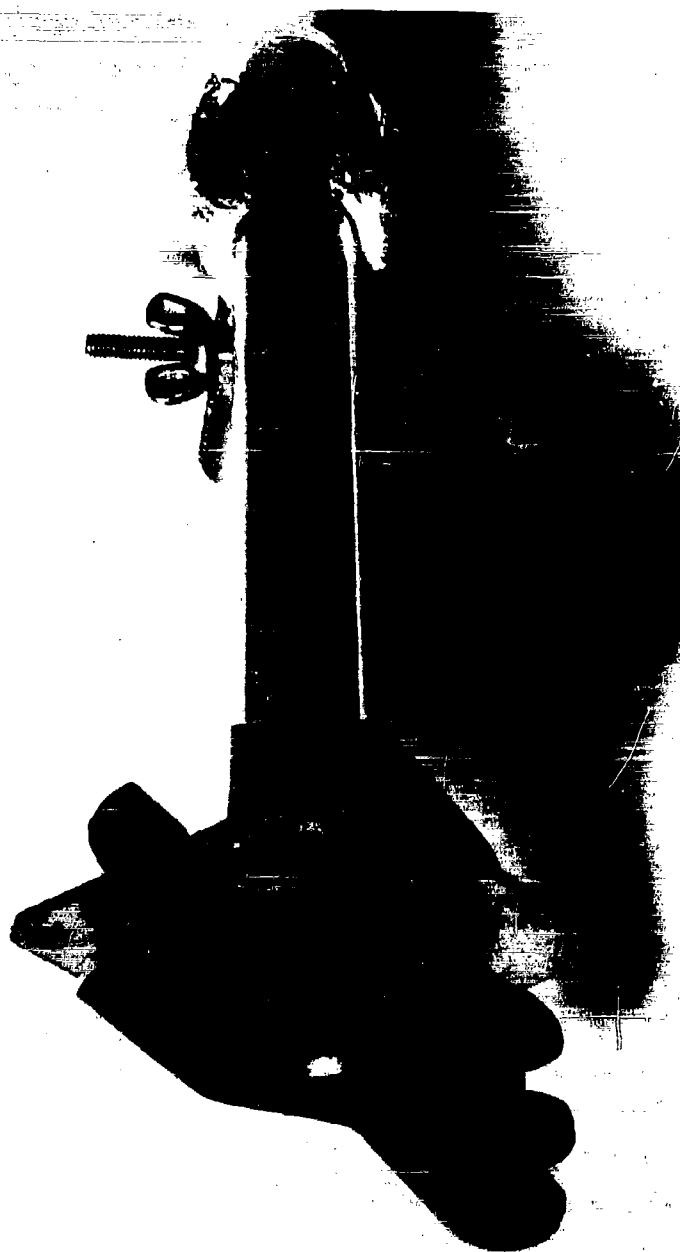
Figure 16 Apparatus for Evaluation of Elastomer Coatings
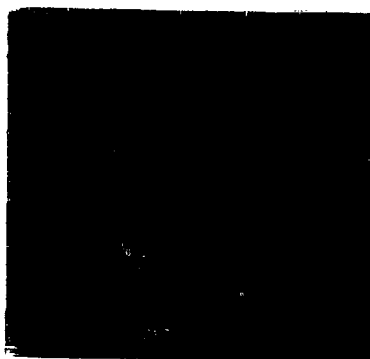
Elastomer · Specimen
No Coating

Uncoated after 72
hr. N_2O_4 Exposure
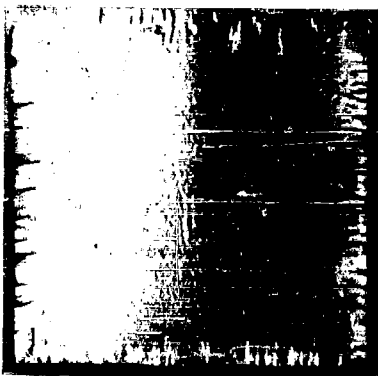
Aluminum Coated
Before N_2O_4 Exposure

Aluminum Coated after
72 hr. N_2O_4 Exposure

Aluminum Coated
with Pinholes after
72 hr. N_2O_4
Exposure

Figure 17 Evaluation of Aluminum Coated Butyl Rubber in N_2O_4

microscopic cracks at low elongations. The replacement of the top surface of the copper by gold (method three) resulted in a satisfactory appearing coating. Permeability studies with N_2O_4 showed the coating to be non-continuous. Electrodeposition of gold on the Shipley copper substrate was accomplished with relative ease but the finished specimen was excessively brittle. An electrochemical technique known as the Dalic process has been investigated because Dalic coats are known to possess low porosity. This varies from metal to metal but, roughly speaking, one half a mil of Dalic plating will be as impermeable as two mils of a similar bath deposit. For example, if a copper strip is plated with gold from a conventional bath on a single side and the strip immersed in nitric acid, the dissolution of the copper in the nitric acid will leave the gold in powder or fragment form. If, however, a Dalic plated deposit is treated in the same way, thickness of gold of less than one micron will give a continuous unbroken sheet of gold with no porosity. There is also an apparent complete absence of hydrogen embrittlement of the metal.

The Dalic gold could not be applied directly on the reduced (Shipley) copper bases metal due to resultant high local heating. This is inherent in the process and especially critical when plating on very thin conductive substrates. The Shipley copper coated elastomer could, however, be electroplated with a flash copper coating. This was to increase the thickness of the copper substrate and to avoid the problem of localized overheating. Dalic gold, as well as standard electroplated gold, could then be deposited onto the bases copper with ease and with no resultant voids due to overheating. However, these coatings were still excessively brittle.

Silver has also been deposited on rubber using the chemical reduction method. These coatings appear continuous microscopically and are conductive; however, the silver is rather easily abraded from the rubber base.

Although many of the metal coating techniques investigated look promising only the rubber-metal laminates yielded continuous, impervious and flexible coatings. These data are summarized in Table XXI.

Conclusions:

These data show various hydrocarbon elastomers which are compatible with hydrazine-type fuels for at least 30 days at

TABLE XXI

TECHNIQUES EVALUATED FOR THE PREPARATION OF METAL-RUBBER COMPOSITES

Technique	Metal	Rubber	Visual Appearance	Remarks
Lamination	Aluminum	Butyl	Very good	Exc. flexibility, static seal to N_2O_4 - 4 wks.
	Aluminum	EPR	---	Poor adhesion
	Aluminum	Viton	---	Poor adhesion
	Gold	Butyl	---	Greater flexibility, poor to fair adhesion
	Gold	EPR	---	Poor adhesion
Vacuum Deposition	Many	Many	Good	Non-continuous or porous
Chemical Reduction	Shipley Cu	Butyl	Good	Attacked by N_2O_4
	Atomex, Oromerse, or Cuposit Gold	Shipley Cu/Butyl	Good	Permeable to N_2O_4
	Brashear Silver	Butyl	Good	Conductive, easily abraded
Electrodeposition	Dalic Gold	Shipley Cu/Butyl	Poor	Voids due to local heating
	Dalic Gold	Atomex Gold/Shipley Cu/Butyl	Poor	Voids due to local heating
	Cu Electroplate Dalic	Shipley Cu/Butyl On above	Good Good	Excessively brittle
	Gold Electroplate	Shipley Cu/Butyl	Good	Excessively brittle

160°F. Several of these elastomers are suitable for static as well as dynamic application. EPR formulation 132 appears to be the best composition for this application. Polar polymers such as Viton and Silastic LS-53 show excessive swelling in N_2O_4. Non-polar hydrocarbon polymers swell considerably less and are suitable for short term application in contact with N_2O_4 at 60-70°F. EPR formulation 132 was found to be compatible with ClO_3F and N_2F_4 /ClO_3F mixtures for at least one week at room temperature. The only elastomer found to be compatible with ClF_3 is nitroso rubber gums; amine cured nitroso rubber is not compatible with ClF_3. Resin coated elastomers are not compatible with N_2O_4. This may be due to imperfections in the coating but it is most likely a result of permeation through the resin coating. Metal encapsulation of elastomers appears promising but has met with only limited success to date.

Acknowledgement:

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Session III

ELASTOMER PROBLEMS IN OUTER SPACE

Chairman: J. M. Kelble
U.S. Air Force

SELF-SEALANTS FOR AEROSPACE VEHICLES

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The future will assuredly bring forth the frequent operation of manned and unmanned vehicles in space environments. The time of operation, radiations of several types, and high vacuum are factors which are generally considered. Additionally, particulate matter exists in space which varies in size from microscopic particles to asteroids. These objects may attain enormous speeds. The possibility therefore exists of collisions of space vehicles with these objects and resulting punctures of the vehicles. The consequences of puncture appears particularly serious in the case of manned vehicles. Ideally, these punctures should be sealed immediately, but the locations may be inaccessable or the punctures may be sustained without immediate knowledge of the occupants.

Therefore, materials and concepts which will provide a self-sealing capability to space vehicles appears highly desirable. Ideally, materials which provide this capability would be:

1. highly reliable
2. low in weight
3. easily incorporated in a variety of designs

Two of the approaches which were investigated to attain this capability appear promising. These were based on a/ a concept which functions via chemical reactions and b/ a concept based on the mechanical properties of elastomeric materials.

EQUIPMENT

A device was needed to evaluate experimental self-sealing systems. This device had to be capable of firing a particle through a test specimen and capable of maintaining a vacuum on one side of the specimen and a substantial pressure on the other.

The action of meteoroids cannot be economically duplicated due to the tremendous speeds involved. The most important consideration, however, is the obtaining of a puncture in a specimen under vacuum conditions. This was therefore taken as the controlling parameter and a Remington* 222 was incorporated into the device. The projectile travels approximately 3500 feet per second.

The "Meteoroid Simulator" that was built is shown in Figure 1. The schematic diagram of the device is shown in Figure 2.

The device consists of three (3) chambers as shown in the schematic diagram. The chambers are eight (8) inch diameter steel pipe, each approximately four (4) feet long. Chamber I contains the rifle. Chamber II is the test chamber where a vacuum is maintained. Chamber III is at atmospheric pressure and contains approximately two (2) feet of sand to act as a backstop for the bullet.

The specimen is mounted between Chambers II and III and Chambers I and II are evacuated. The rifle is fired and the bullet passes through Chamber II, the test specimen, and is caught by the backstop. Gases from the explosion of the cartridge are bled off the barrel of the rifle. and actuate a switch which closes the valve between Chambers I and II. There is then a vacuum on one side of the specimen, atmospheric pressure on the other side, and a puncture through the specimen. The vacuum side of the specimen can be viewed through the viewing port. Sealing of a specimen is determined by the manometer.

DOUBLE HOLLOW WALL CONCEPT

Initial effort was expended on determining the materials to be used for the specimens. That is, the materials to serve as the walls rather than the sealant. Elastomers, plastics, and metals were evaluated. It was found that the combination of a thin aluminum sheet (16 mils thick) cemented onto a rubber sheet (75 mils thick) gave the type of specimen that was desired. The projectile in going through the aluminum side first, left a hole approximately 0.075 inch in diameter in the rubber. The hole size is reduced in this configuration because the rubber elongates before puncture and a lesser amount of rubber is removed in the stretched condition than would be in an unstretched condition. This mitigated the initial sealing problem since it would be easier to seal a 0.075 inch hole than a .22 inch or larger hole. Once the technology for sealing the smaller hole is available, it can be used in attempts to seal larger holes.

Room temperature vulcanizing silicone sealants were mixed with dibutyl tin dilaurate (DBTDL) and stannous octoate as catalysts. Both catalysts caused cure of the sealants. DBTDL is much slower than the stannous octoate - 30 minutes as opposed to one minute. The

* Remington Arms Company, Incorporated.

FIGURE 1. Meteoroid Simulator
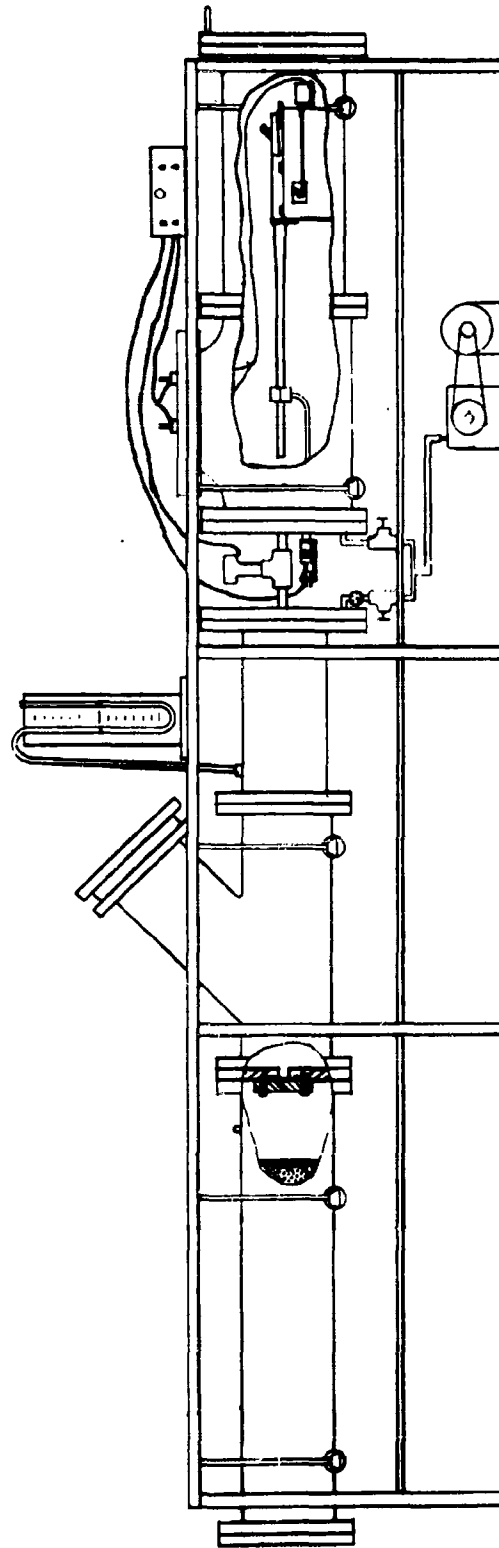
FIGURE 2. Meteoroid Simulator (Schematic Diagram)

relative amount of catalyst used was usually small - 4 parts to 100 parts sealant. The resultant cured materials looked to be good candidates for self-sealants.

A polypropylene oxide-toluene diisocyanate adduct identified as P1010-TDI (see Figure 3) was investigated for rapid crosslinking with various amines. P1010-TDI is a fluid material very similar to honey in both viscosity and color. The sample was 70 percent solids and contained a 50/50 mixture of toluene and cellosolve acetate as solvent. Molecular weight of the adduct is approximately 1300 and the viscosity is approximately 16,000 centipoises.

Ethylene diamine, triethylene tetramine, tetraethylene pentamine, and hexamethylene diamine made into a 70 percent solution with water were mixed with P1010-TDI (70%) in a ratio of 5 parts to 100 parts. All caused immediate gellation. The reaction is so fast that the materials cannot be well mixed.

The P1010-TDI (70%) material appeared preferable for subsequent self-sealant evaluations over the silicones because the reaction is faster and the resultant product is stronger.

As materials were available that would quickly change from fluids to a solid upon mixing, the problem then became the separation and mixture of these materials when punctured in the "Meteoroid Simulator."

One way of doing this would be by use of a double hollow wall. The two fluids would be separated by a thin impermeable membrane. Upon puncture the fluids would flow toward the vacuum and would mix together forming a solid, plugging the puncture. Specimens were prepared as shown in Figure 4. The component parts are cemented together with a synthetic rubber base adhesive. When evaluated in the "Meteoroid Simulator" the aluminum sheet is toward the vacuum and the back wall toward atmospheric pressure. The projectile passes through the aluminum first and the fluids are forced toward and through the aluminum and rubber wall by the pressure maintained on the back of the specimen.

The first specimens prepared used a buna-N vulcanizate as the first wall and aluminum sheet (16 mils thick) as the separating wall and back wall. One specimen contained P1010-TDI (70%) as Fluid A and ethylene diamine as Fluid B. The other contained an unfilled silicone sealant as Fluid A and stannous octoate as Fluid B. Both specimens had tremendous holes in the separating and back walls of approximately 1 inch in diameter. There was crosslinking of both sealants but it was quite obvious that another material would have to be used for the walls.

Four additional specimens using the same fluids were prepared. These were:
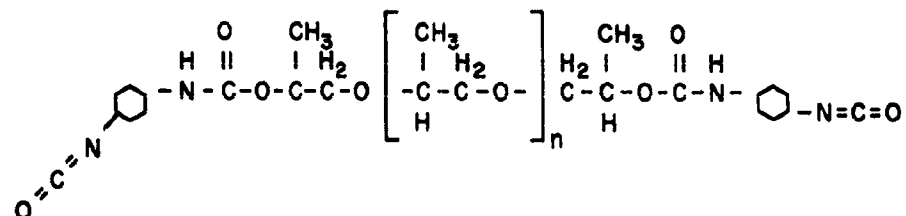
POLYPROPYLENE OXIDE-TOLUENE DIISOCYANATE ADDUCT
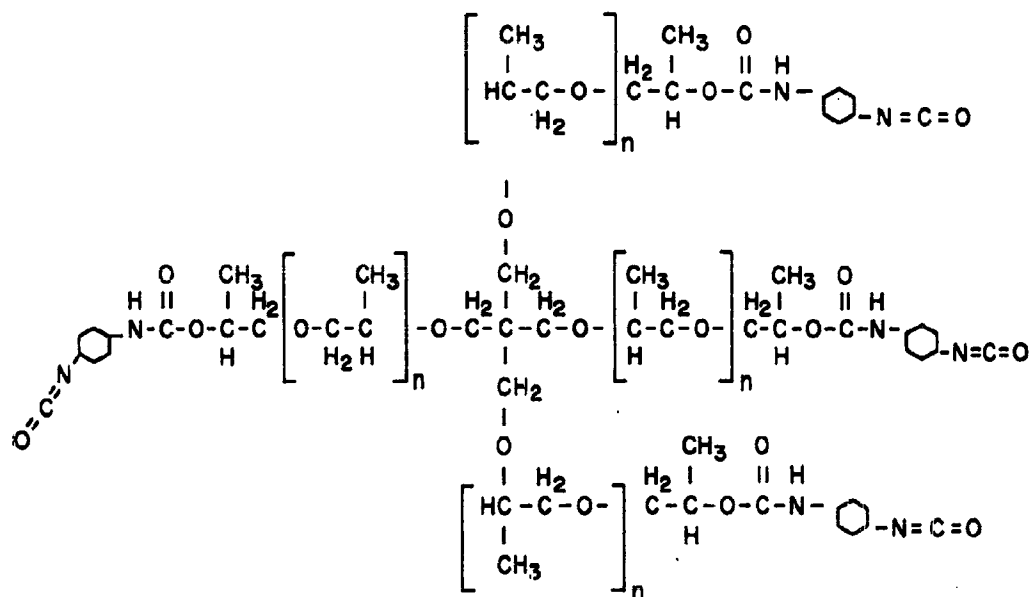
PENTAERYTHRITOL BASED
POLYOXYPROPYLENE POLYOL-TOLUENE DIISOCYANATE ADDUCT

FIGURE 3. Urethane Prepolymers

134

Aluminum sheet

Rubber sheet

Rubber sheet with hole in
center serving as shim

Fluid A

Separating wall

Fluid B
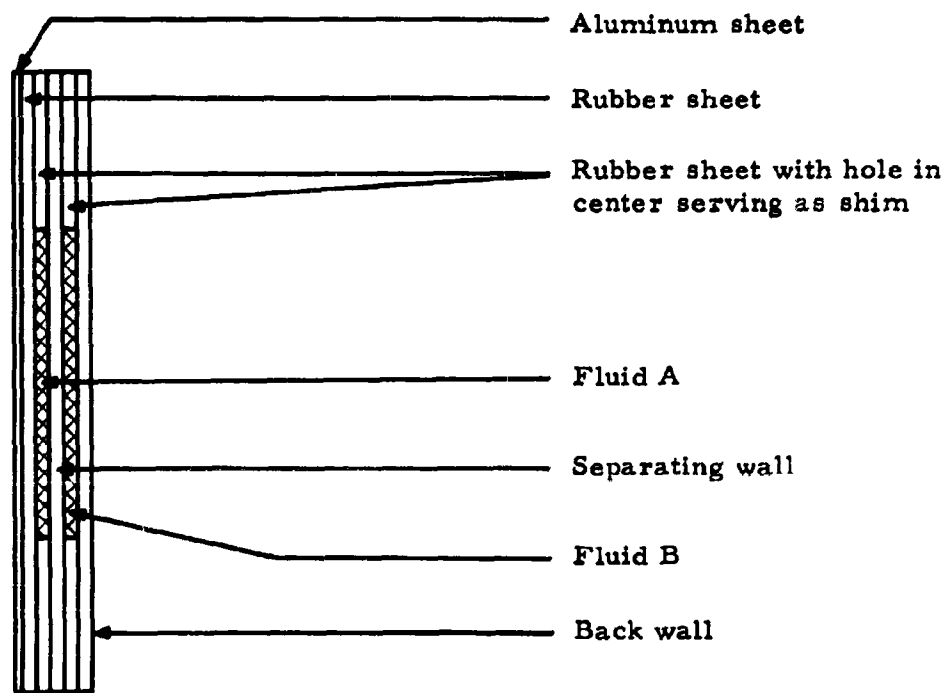
Back wall

FIGURE 4. Double Hollow Wall Sealant Specimen

135

1. P1010-TDI (70%), ethylene diamine, 1.5 mil aluminum foil as separating wall, buna-N vulcanizate as back wall.

2. P1010-TDI (70%), ethylene diamine, buna-N vulcanizate as separating and back wall.

3. Silicone sealant, stannous octoate, 1.5 mil aluminum foil as separating wall, buna-N vulcanizate as back wall.

4. Silicone sealant, stannous octoate, buna-N vulcanizate as separating and back wall.

The P1010-TDI (70%) flowed out through the hole toward the vacuum with both the aluminum foil and the buna-N vulcanizate as the separating wall and the silicone sealant flowed out with the buna-N wall. All three of these slowed the leakage of air through the puncture considerably. The silicone sealant with the aluminum foil separating wall did not flow out and no seal was obtained. It was interesting to note that the aluminum foil tore, allowing a large amount of catalyst or crosslinking agent to come into contact with the sealant immediately whereas the rubber wall exhibited a small hole allowing the agent to pass through more slowly. It would seem that the latter case is preferred since the sealant is given more time to flow toward the puncture before solidifying.

Ethylene diamine was found to be so volatile that after firing the test chamber was filled with the vapor and work with this amine was stopped.

The crosslinking agent was changed to a 70 percent solution of hexamethylene diamine (HMDA) in water. Four specimens were then prepared using P1010-TDI (70%) and HMDA (70%). Two of the specimens had aluminum foil as the separating wall and the other two had a buna-N vulcanizate as the separating wall. One of each contained glass fiber matting in the same cavity as the P1010-TDI (70%). The purpose of the matting was to give added strength to the crosslinked materials and perhaps immediately bridge over the puncture to give the solid material something upon which to attach.

The two specimens without matting did not seal. The one with the buna-N vulcanizate wall extruded slightly out the hole toward the vacuum and slowed the leakage slightly. The one with the aluminum wall showed no indication of sealing whatever. It appeared once again that the buna-N vulcanizate separating wall was superior to the aluminum foil.

Neither of the specimens with glass fiber matting sealed. Upon disassembling the specimens it was found that the sealant was not cured. Evidently the matting restricted the flow of the constituents and did not allow proper mixing for curing.

Three specimens were prepared containing the following as Fluid A:

1. Pentaerythritol based polyoxypropylene polyol-toluene diisocyanate adduct - 400 molecular weight, identified as PeP 450-TDI (see Figure 3).

2. P1010-TDI (70%) with 25 phr titanium dioxide

3. P1010-TDI (70%) with 5 phr Cab-O-Sil*

Fluid B in all cases was HMDA (70%). PeP 450-TDI was used because it was more reactive than P1010-TDI (70%) and it was felt that a stronger resultant material would be obtained.

Upon firing, specimen 1 sealed immediately and specimen 2 sealed after the vacuum had decreased by approximately 9 inches of mercury. Specimen 2 leaked slowly until the puncture was covered momentarily. This gave the material a chance to set and seal the puncture. Specimen 3 exhibited a slight persistent leak. These results were, of course, quite encouraging.

These evaluations were then repeated in order to determine reliability. Four additional specimens were prepared. Two of these contained PeP 450-TDI as Fluid A, one contained P1010-TDI (70%) with 25 phr titanium dioxide, and the other contained P1010-TDI (70%) with 35 phr titanium dioxide. Fluid B was HMDA (70%) in all cases. Unfortunately, none of these specimens displayed any indication of sealing. A new type rubber sheeting had been used for the wall materials of these specimens which was based on neoprene. It was noticed that the holes in the wall materials were larger than had been obtained with the buna-N. Physical property evaluations were made on the neoprene sheet and the following were obtained:

Tensile Strength	1000 psi
Elongation	280%
Hardness	52 points

The buna-N that had been used previously had a tensile strength of approximately 3300 psi, an elongation of 400 percent, and a hardness of 70.

The change in wall material was one reason for nonreproducibility, but was not the only reason. Two more specimens were prepared with PeP 450-TDI as Fluid A and HMDA (70%) as Fluid B. Both specimens had buna-N vulcanizate walls but neither sealed. It thus appeared that the good results could not be reproduced without further research into the mechanism of sealing and further refinements to the evaluation specimens.

* Product of Godfrey L. Cabot, Inc.

It was believed that possibly the crosslinking agent was passing through the sealant too quickly when going toward the vacuum and was not making sufficient contact for solidification. More viscous crosslinking agents were obtained and mixed with PeP 450-TDI. These were Polyamine T*, Trimine Base**, and stannous octoate mixed with Quadrol***, and hexamethylene diamine carbamate mixed with HMDA (70%). All caused curing of the PeP 450-TDI but none were as fast as with the less viscous crosslinking agent.

Six specimens were then prepared, all with PeP 450-TDI as Fluid A. Fluid B was:

1. Quadrol with 2 percent stannous octoate

2. HMDA (70%) mixed with titanium dioxide to form a paste

3. Polyamine T

4. HMDA (70%) mixed with HiSil X303**** to form a paste

5. HMDA (70%) in glass fiber matting

6. HMDA (70%) in cotton gauze

None of these specimens sealed. Curing was noticeably slower and when curing did take place the sealant was weaker than had been obtained with the less viscous crosslinking agents.

Results indicated that the very liquid crosslinking agent was necessary for getting adequate mixing of the constituents and rapid solidification. The PeP 450-TDI was not satisfactory for practical use in this application, as the material reacted with the atmospheric moisture during preparation of samples. It was therefore decided to return to the use of P1010-TDI (70%). The amine affected the bond between the component parts of the test specimen and sometimes the amine would leak from the sample before firing. This problem was solved by heat sealing the amine into small polyethylene bags. Also, it was felt that the water in the crosslinking agent (HMDA) that was being used might be causing some foaming and a liquid amine would be better. Therefore, triethylene tetramine (TETA) was used in subsequent samples.

Immediate success was obtained by incorporating these changes. Three specimens were prepared all of which contained TETA as Fluid B. Fluid A was as follows:

* Product of Union Carbide Chemicals Company
** Product of Naugatuck Chemical
*** Product of Wyandotte Chemicals Corporation
**** Product of Columbia Southern Chemical Corporation

1. P1010-TDI (70%) with 10 phr Cab-O-Sil

2. P1010-TDI (70%) with 7.5 phr Cab-O-Sil

3. P1010-TDI (70%) with 35 phr titanium dioxide

Specimen 1 sealed immediately with a ball of material extruded out the puncture into the vacuum chamber of approximately 1/4 inch in diameter. Specimens 2 and 3 did not seal but reduced the puncture to a very slow leak.

Some previous work had used a thin rubber coated fabric as the back wall. It was noted that the coated fabric had been torn but not as severely as had the aluminum foil. It was felt that perhaps more amine in the sealant would be advantageous. In addition, the coated fabric was quite lightweight and this would reduce the weight of the structure incorporating this system.

Four more specimens were prepared using TETA as Fluid B. Fluid A was:

1. P1010-TDI (70%) with 10 phr Cab-O-Sil - 1000 psi neoprene as separating wall

2. P1010-TDI (70%) with 10 prh Cab-O-Sil - Coated fabric as separating wall

3. P1010-TDI (70%) with 7.5 phr Cab-O-Sil - Coated fabric as separating wall.

4. P1010-TDI (70%) with 35 phr titanium dioxide - Coated fabric as separating wall.

Specimens 1 and 3 slowed the leakage but none of the specimens sealed. It was apparent that inconsistencies still existed and these would have to be worked out of the system. It was noted that sometimes the same formulation would extrude and sometimes it would not extrude and extrusion is essential for sealing. Evidently, a slight amount of pressure is desirable to insure this extrusion and for this reason the cavity containing Fluid A was filled to excess in subsequent specimens. This causes a slight stretching of the separating wall, and so exerts a slight pressure. Also, it must be realized that the test specimens are fired through in a vertical position and the sealant flows to the bottom of the specimen before firing. Therefore, sufficient sealant must be present to insure sealant at the point of puncture.

Three additional specimens were prepared. All contained the coated fabric as the separating wall, the 1000 psi neoprene sheet as the back wall, and TETA as Fluid B. Fluid A was:

1. P1010-TDI (70%) with 10 phr Cab-O-Sil

2. P1010-TDI (70%) with 7.5 phr Cab-O-Sil

3. P1010-TDI (70%) with 50 phr titanium dioxide

None of these specimens sealed. They had all been filled to excess with Fluid A, however, no extrusion had taken place. Large holes were present in both the separating wall the the back wall. It was definitely decided that the 1000 psi neoprene sheet was unsuitable for the back wall and that the 3000 psi buna-N sheet was necessary.

The best material for the separating wall had to be determined. Three specimens were prepared using the 3000 psi buna-N sheet for the front and back wall. Fluid A was P1010-TDI (70%) with 10 phr Cab-O-Sil and Fluid B was TETA. The separating wall was coated fabric in the first specimen, 1000 psi neoprene in the second, and 3000 psi buna-N in the third. The specimen with the coated fabric did not seal. There was no extrusion of the sealant but a large amount of the TETA escaped into the vacuum chamber. The specimen with the 1000 psi neoprene reduced the puncture to a slow leak. There was slight extrusion and the specimen appeared to be approaching a complete seal. The specimen with the 3000 psi buna-N extruded a ball of solid material approximately 3/8 inch in diameter. There was some bubbling at the top of the ball which indicated slight leakage. This bubbling ceased in 15 to 20 minutes and the specimen was then sealed. It was thus apparent that all three walls should be of the 3000 psi buna-N sheet and work was necessary for further characterization of the sealant.

Three identical specimens were then prepared except for a variation of amount of filler in the sealant. All specimens contained aluminum sheet, 3000 psi buna-N sheet as walls, and TETA as Fluid B. Fluid A was P1010-TDI (70%) with 7.5, 10, and 12.5 phr Cab-O-Sil. The specimen containing 7.5 phr Cab-O-Sil had a great deal of extrusion but there was still a fast leak. Upon examination, the ball of extruded material was not adequately adhered to the test specimen. The specimen with 10 phr Cab-O-Sil reduced the puncture to a slow leak. There was only very little extrusion. The specimen with 12.5 phr Cab-O-Sil also had very little extrusion and reduced the puncture to a slow leak. It appeared that the ideal formulation was between 7.5 and 10 phr Cab-O-Sil.

Specimens were prepared with 8 and 9 phr Cab-O-Sil. The specimen with 8 phr sealed immediately. The specimen with 9 phr Cab-O-Sil reduced the puncture to a slow leak and appeared to be approaching a complete seal.

Several other specimens have been prepared using 8, 8.25, and 8.5 phr Cab-O-Sil in the P1010-TDI (70%). No real failures have been obtained. Two specimens did show a loss of vacuum after puncture

but the loss was so slight that it was not determined if the loss was through the puncture or at some other place such as between the specimen and the vacuum chamber.

A specimen of P1010-TDI was received that was 100 percent solids. This was very similar to the 70 percent solids material. Viscosity of the 100 percent solids material was approximately 18,500 centipoises. It was believed that a lesser amount of Cab-O-Sil would be needed for comparable sealant specimens. Experimentation showed, however, that the optimum amount of Cab-O-Sil was unchanged from previous formulations with the 70 percent solution of P1010-TDI.

Work is continuing to further refine this concept. An oil diffusion pump is being incorporated into the "Meteoroid Simulator" for obtaining high degrees of vacuum. New specimen holders have been fabricated which will permit the bolting together of individual walls and eliminate the use of adhesives, and will expedite the evaluation of self-sealing materials. The "Meteoroid Simulator" has been modified so that high speed motion pictures in the range of 25,000 frames per second can be taken of the bullet as it punctures the specimen and the sealant immediately thereafter. This should assist greatly in better understanding the mechanisms of self-sealing.

ELASTOMERIC LAMINATES

Before proceeding with a detailed explanation of the ideas behind this general concept, the behavior of materials on puncture by particles at common speeds (e.g., up to 4000 feet per second) is worthy of consideration. In this discussion, it is assumed that the penetrating particle will be undeformed.

Brittle materials will result, on puncture, of holes of at least the size of the penetrating object. In many cases, the hole will be greatly larger than the penetrating object or may generate cracks extending large distances from the point of puncture.

Ductile materials generally result in holes of the order of the size of the penetrating object.

Elastomeric materials, however, may result in holes considerably smaller than the penetrating object. A cursory explanation presents itself if it is assumed that the puncture is caused by a sharp object which removes little, if any, of the elastomeric material on puncture. Some reflection, however, indicates that a similar effect can be obtained if on impact the piercing particle causes removal of an amount of elastomeric material equal to its own cross-section. This is illustrated in Figure 5. Here, prior to contact with the penetrating object, the elastomeric material is present with an initial thickness of t_0. As the penetrating object comes in contact with the elastomeric material, a substantial distortion of the elastomeric material occurs prior to puncture. (This phenomena has

141
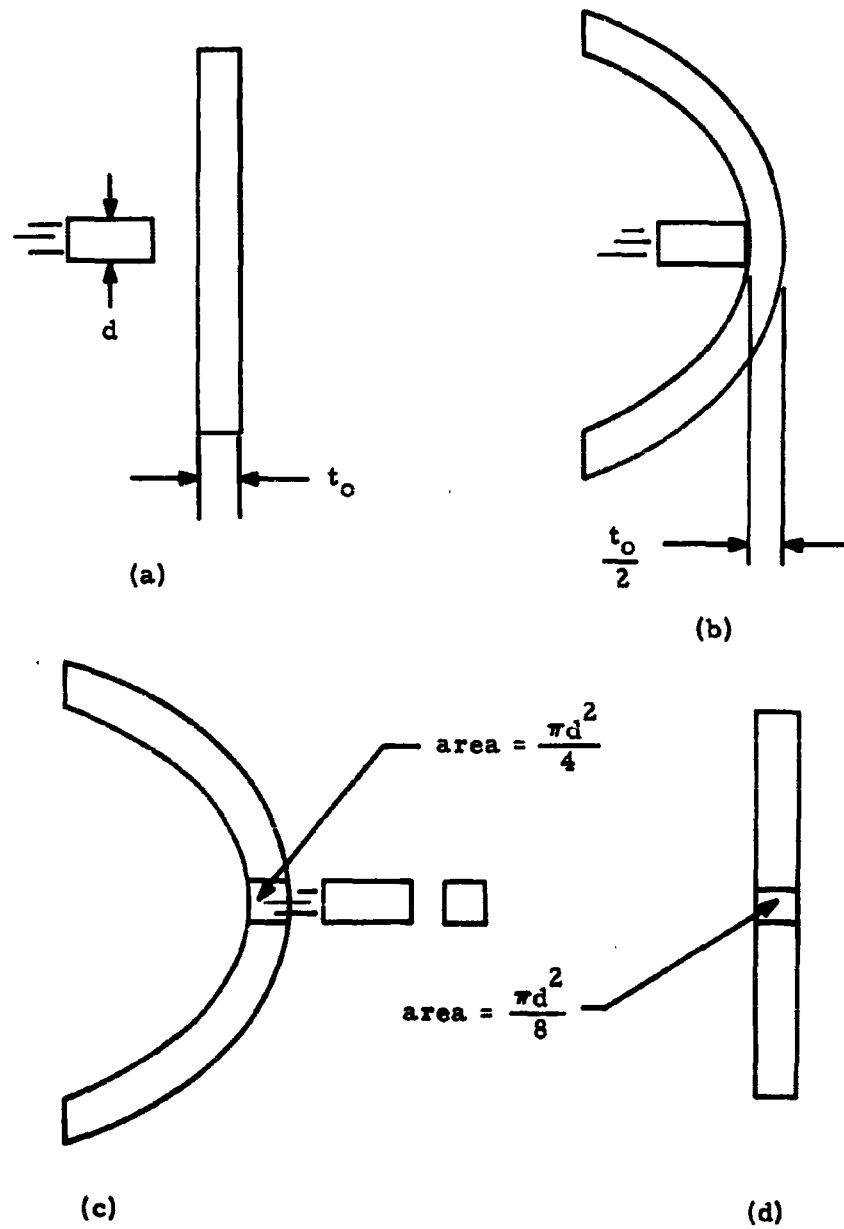
FIGURE 5. Low Speed Projectile Penetration of Elastomeric Material

been observed repeatedly on a qualitative basis.) If the elastomeric material is assumed to be distorted to a hemispherical configuration prior to puncture, a rough approximation would indicate that on return to the original position the hole would be of about 50 percent of the area of the cross-section of the penetrating object. As the area of a hemisphere is:

$$A_H = 2 \pi r^2$$

and the original area of the plane surface is:

$$A_p = \pi r^2$$

it is apparent that the average thickness of the elastomer when distended to a hemispherical shape is half the original thickness, or $d_0/2$. Hence, when a plug of material is removed when the elastomeric material is distended, a return to the normal (planar) configuration results in a retraction as previously stated. Obviously, distortions yielding even greater reductions in thickness prior to penetration will leave even smaller holes on return to normal configurations.

Hence, for low speed penetrating particles, a system of elastomer materials is:

1. highly reliable in reducing the size of the hole resulting from puncture

2. low in weight

3. easily incorporated in a variety of designs

In order to be of value to vehicles and stations in space, the system must also be effective for very high speed particles. While a reduction in size of holes from punctures obviously would reduce the rate of loss of contained fluids, complete reduction of hole size (that is, elimination) is far more desirable.

Extensive research is currently underway to investigate the effects of impacts of very high speed particles on various materials. As yet, the speeds of particles in the solar system have not been duplicated in the laboratory. However, it appears logical that on very high speed impacts, no substantial distortion of the punctured material will occur at significant distances from the point of impact. Very briefly, this is attributed to the short time involved during impact and the inertia of the punctured material.

Since high speed impact of objects with elastomeric materials are not expected to yield but a very localized distortion, we are at a seeming impasse. However, reflection (on at least a theoretical basis) yields some hope. The reduction in puncture area from low speed objects of elastomeric materials was attributed to a substantial distortion prior to actual puncture. This distortion is, of course, a

two dimensional extension. But two dimensional extension is equivalent to one dimensional compression. In an extremely broad sense, it can be stated that if an elastomeric object is distorted from its normal form, the energy contained within the object is independent of the history of how the distortion was accomplished. This assumes that no chemical changes have taken place.

Hence, it can be hypothesized that punctures induced by very high speed projectiles of strained elastomeric materials without distortion would be expected to yield puncture area reductions on relaxation comparable with those obtained with low speed punctures where dimensional extension occurs prior to puncture. But how can strained elastomeric material be practically attained and maintained? Certainly the direct compression of objects of large area present formidable practical problems.

The use of laminated sections of elastomeric materials offers a potential solution. Composites of a minimum of three members appear necessary to achieve laminated structures which at equilibrium have no curvature. These laminates consist (at the time of assembly) of: 1/one inner membrane under biaxial tension bonded to two external neutral (unstressed) members, or 2/ two external members under biaxial extension bonded to one minor neutral member (see Figure 6).

The figures are admittedly highly schematic. For specimens in which the height is significant in relation to the dimensions of the horizontal plane, the edge defects would be quite large. Hence, these specimens are better thought of as representative of the center portions of larger specimens.

These laminates will be examined using the following equations:*

1. for simple elongation,

$$f = G(\lambda - 1/\lambda 2)$$

2. for uniform two dimensional extension

$$t_1 = t_2$$
$$t_3 = 0$$
$$\lambda_1 = \lambda_2 = \lambda$$
$$\lambda_3 = \lambda^{-2}$$
$$t_1 = G(\lambda^2 - \frac{1}{\lambda^4})$$

* L. R. G. Treloar, The Physics of Rubber Elasticity, 1958.
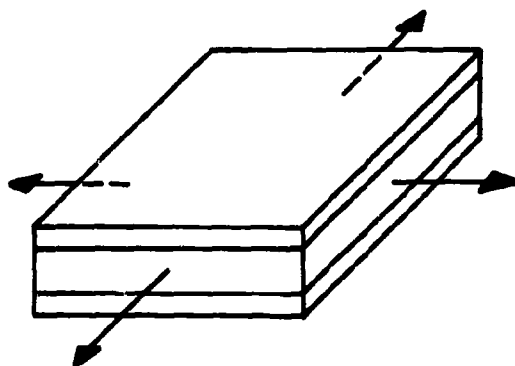
a) Laminate prior to bonding inner
    member stressed outer members
    neutral
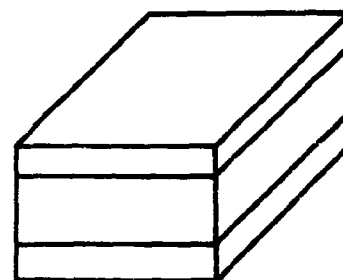
b) Laminate a) at
    equilibrium
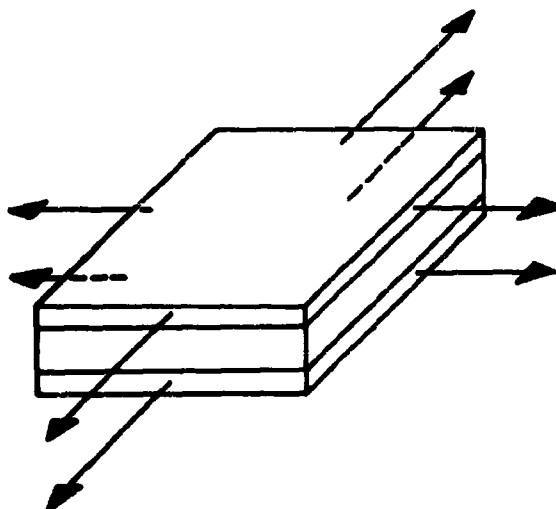
c) Laminate prior to bonding outer
    members stressed inner member
    neutral
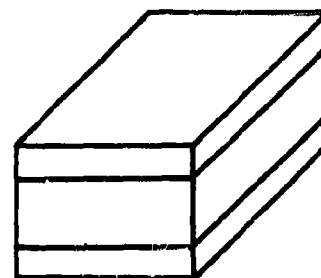
d) Laminate c) at
    equilibrium

FIGURE 6. Schematic Assembly of Elastomeric Laminates

145

3. for undirectional compression

$$f_o = G(-\frac{1}{\lambda_3^2} - \lambda_3)$$

where:

f = force per unit cross-secional area measured in the unstrained state

G = modulus

λ = extension ratio

t = stress referred to the strained dimension

In the first case of Figure 6, the inner member of area A_i and thickness d_i in the **unstrained** state is biaxially extended·to an area $2A_i$ and thickness $d_i/2$. **This** member is then bonded to two external members of area $2A_i$ and thickness d_e. All members are of the same material and, hence, have the same modulus G. If we now remove the forces which have extended the inner member to the area $2A_i$, what dimensions will the bonded laminate assume? As the structure is balanced in the x and y planes, no curvature will result. The final area of the structure will obviously lie between A_i and $2A_i$. The final area is also dependent upon the thicknesses d_i and d_e.

The outer members will decrease in the x and y dimensions and increase in the z diminsion, and are, hence, similar to the distortion produced in simple elongation. Assuming this, the force in each external member (at equilibrium) is:

$$f = G(\lambda - 1/\lambda^2)$$

If A_i is defined as a unit area, and two outer members are involved, the total force accompanying the simple extension of these outer members becomes

$$f_o = G(\lambda - 1/\lambda^2) \frac{2A_i}{A_i} \quad (2)$$

$$f_o = 4G(\lambda - 1/\lambda^2)$$

Now the inner member (which at the time of assembly of the laminate has an area of $2A_i$) has decreased in thickness by one-half. Thus:

$$\lambda_3 = 0.5$$
$$\lambda_3 = \lambda^{-2}$$

or,

$$0.5 = \frac{1}{\lambda^2}$$

and,

$$\lambda^2 = 2$$

$$\lambda = \sqrt{2} = 1.41 \text{ (the x + y dimensions)}$$

Assuming square specimens, the total force of the inner member becomes

$$f_e = G(\frac{1}{\lambda_3^2} - \lambda_3)$$

For a laminate in which the volume of the inner member is equal to the sum of the volumes of the outer members, the unstrained measurements are:

for the two outer members

   area $= 2A_i$

   thickness $= d_i/4$

for the inner member

   area $= A_i$

   thickness $= d_i$

thus:

$$2(2A_i \times \frac{d_i}{4}) = A_i \times d_i$$

The total force developed in both external members of the laminate is:

$$F_e = 2(2A_i)(G)(\lambda - \frac{1}{\lambda^2})$$

and

$$\lambda = \frac{d_{is}}{d_i/4}$$

where: d_{is} = the thickness of the external members at any extension.

The total force developed prior to release of the inner member of the laminate is:

147

$$F_i = 2(\ 2A_i)(\frac{d_i}{2})(G)(\ \lambda^2 - \frac{1}{\lambda^4}$$

where:

$$\lambda = \frac{\sqrt{2A_i}}{A_i} = \sqrt{2}$$

Thus on release of the assembled laminate, the force developed by the inner member will decrease as the assembly shrinks in area, and the forces developed in both outer members will increase. Beginning with an area of $2A_i$, a plot of F_e and F_i versus decreasing area should give, at the intersection of these curves, the area of the laminate at equilibrium. Since only the relative, and not absolute, forces of the inner and external members determine the final configuration, calculations can be simplified by allowing G, A_i, and d_i to equal unity.

The plot shown in Figure 7 indicates an equilibrium area of 1.58 A_i. This is a reduction at equilibrium to 79 percent of the area at the time of assembly of the laminate. As the area of all the members has decreased by 21 percent, the thickness correspondingly must increase by 27 percent as:

$$2A_i \times d_i = 1.58\ A_i \times d$$

$$d = 1.27\ d_i$$

Similar calculations can be made for a variety of laminates. However, it is necessary that to avoid curvature (at least theoretically) in the laminate at equilibrium the number of stressed members must differ from the number of neutral members (at the time of assembly) by one.

Hence, it appears possible to fabricate sheets of elastomeric materials via the use of laminating techniques in which the members of the laminate are alternately in tension and compression in a direction normal to the plane of the laminate.

With the feasibility of elastomeric laminates indicated from theoretical considerations, the next logical step is to calculate the behavior of the laminates on extreme speed punctures. Unfortunately, this does not appear practical for a variety of reasons, some of which are:

1. The equations used do not describe the stress-strain properties of most elastomeric vulcanizates well over a wide range of distortions. The equations describe the theoretical behavior of gum and not reinforced vulcanizates.
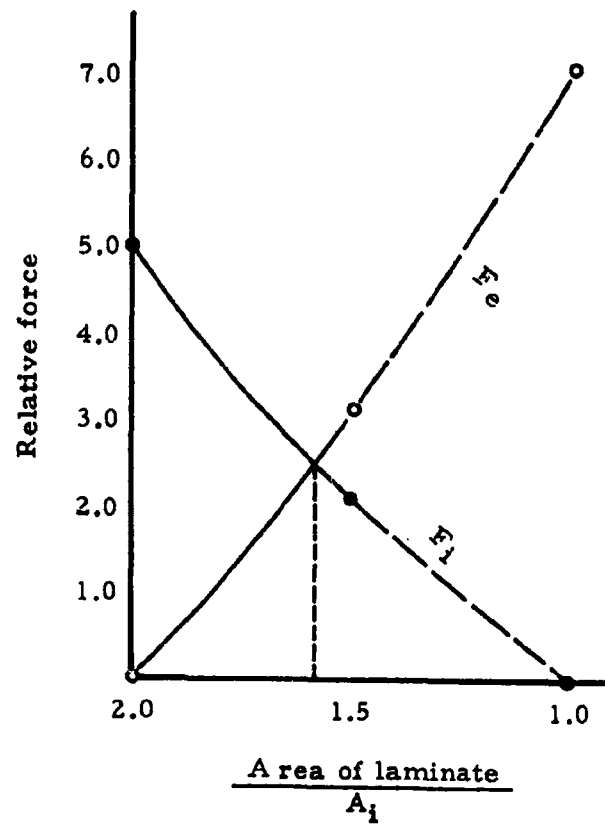
FIGURE 7. Forces in Inner (F_i) and Outer (F_e) Members

2. Stress relaxation, particularly over long periods of time, is neglected by the equations.

3. The contribution of the adhesives used in the assembly of the laminates is neglected.

4. The nature of the puncture (that is the geometry) of elastomeric materials by projectiles of extreme speed is not presently known.

Hence, a more expedient route to evaluate the value of this concept appeared to lie in experimentation.

EXPERIMENTAL

A number of specimens were prepared by subjecting the two outer members of a three ply laminate to biaxial tension with subsequent adhesion to an inner neutral member (see c. and d. of Figure 6). As this series of experiments was preliminary in nature, no rigorous selection of materials was employed. Thus, with materials at hand, a number of three ply laminates were evaluated.

Initially, some of the laminates were subjected to puncture of a 0.22 inch diameter projectile at about 3500 ft/sec. velocity with an air pressure differential of approximately 750 mm Hg maintained across the specimen prior to puncture with the apparatus discussed previously. The self-sealing ability of various specimens was then determined by the rate at which the pressures equalize. None of the elastomeric laminates provided a complete seal, but the better laminates reduced the rate of pressure equalization to very low values. But this type of experiment has the limitation that the deformation on puncture of the laminate is unknown.

Hence, a second type of evaluation was devised in which no distortion of the laminate takes place during puncture. This was done by cooling the laminate in liquid nitrogen, and then drilling (in a stream of liquid nitrogen) holes of various diameters. As the laminates were literally hundreds of degrees below the glass transition temperature, the punctures were effected without distortion. On warming to room temperatures, the forces built into the laminate come again into being. Observations of this type of evaluation were largely qualitative, but were thought to be highly informative.

Typical laminates were prepared with area increases of the areas of the outer members of 300 to 500 percent. Inner members (neutral at the time of assembly) were compresed of a number of low moduli material including closed cell elastomeric sponges.

After chilling in liquid nitrogen, holes of a variety of sizes up to 0.125 inches in diameter were drilled. On warming to room temperature, the area of some of the holes were found to be
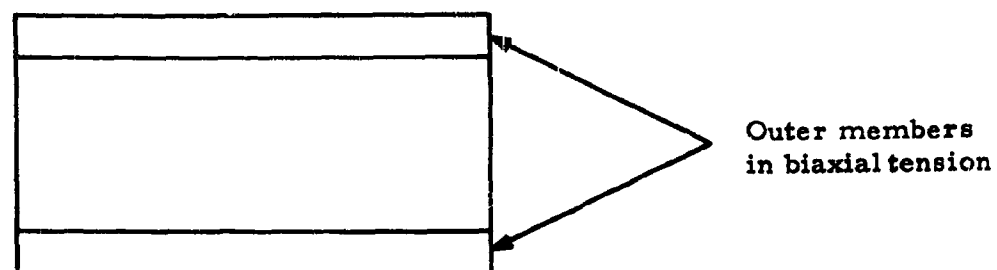
a) Initial laminate
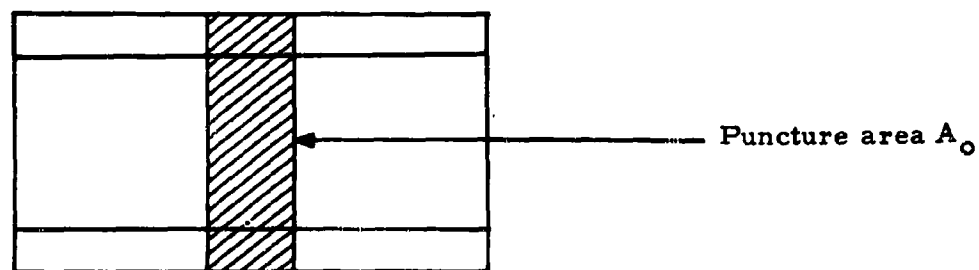
b) Laminate cooled in liquid
nitrogen and puncture drilled
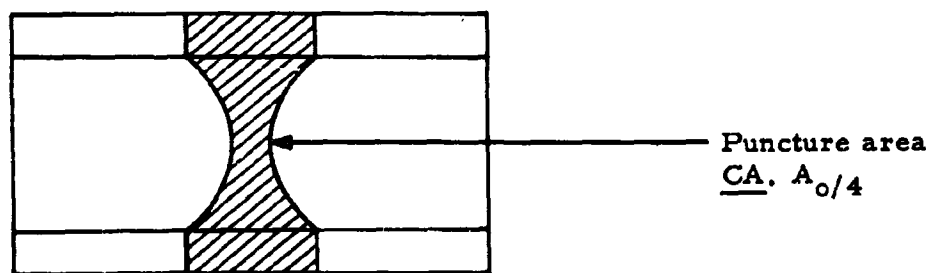
c) Punctured laminate at room
temperature

FIGURE 8. Schematic Cross-Sectional Views of Elastomeric Laminates

reduced by about 75 percent (see Figure 8). However, it was noted that the area of the punctures of the outer members increased considerably, as would be expected. This retraction of the outer members from the axis of puncture thus tends to inhibit the self-sealing action desired of the inner member.

Elastomeric closed cell sponges as inner members were utilized in some cases to obtain laminates in which the inner member would be thick in relation to the outer members because of the comparatively low moduli of the sponges. As considerable amounts of filler and plasticizer were used in compounding of the sponges, stress-relaxation of the inner member seemed considerable. Further, closed cell sponges are not incompressible, and, hence, stress-strain characteristics are not reflected on a theoretical basis by the equations discussed earlier. Hence, even the general design of experimental specimens is largely an Edisonian technique. In spite of these difficulties, sponges were effective in reducing the areas of puncture by 60 to 70 percent. After puncture, the retraction of the members in biaxial tension from the axis of puncture was found to be particularly severe.

The adhesion of flexible high modulus materials (such as fabrics) to the outer members seems promising in mitigating this retraction.

SUMMARY

Efforts are continuing to further evaluate this concept and are currently centered about the design of equipment which will permit the biaxial extension of specimens over wide ranges conveniently. The use of specimens which utilize thicker cross-sections at the clamping sites seems promising to eliminate the frustration which accompanies large extension of simple sheets. A variety of adhesive systems are also being considered.

LOW-FRICTION RUBBERS

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Quantum's participation in the Bureau of Ships' research program has been in the development of high-lubricity surface properties on elastomeric materials.

Worded this way, the goals of the program sound quite earthly and unexciting. But, when interpreted in more popular terms, these goals take on high glamor -- since to develop high-lubricity surfaces on elastomeric materials one, in effect, has to create a paradox of nature.

Speaking in lay language, Quantum's work for the Bureau of Ships has involved development of a "slippery" rubber.

The semantic contradiction is immediately apparent. As everyone knows, rubber derives its name from the fact that it "rubs"- or has high frictional properties. One of the main reasons that rubber is successful in automobile tires is that it rubs -- or, in other words, provides the frictional properties required for traction and for braking. When one talks about imparting slipperiness -- or a low coefficient of friction -- to rubber, he is essentially talking about effecting a complete switch in a basic characteristic of the material.

Now, why would anyone want to take from a useful material a property that has made it valuable in many applications? What is the reason for creating a paradox of nature?

The reason is simply this: In many applications -- particularly those of interest to the Bureau of Ships -- the frictional properties of rubber are valueless; in fact, are totally negative. In an O-ring that retains the lubricant in the bearing area of a rotating shaft -- or in a submarine hatch or rocket launching seal -- or in a rubber bearing -- no one wants high rubbing or frictional qualities. In these and many other applications, the flexibility of

rubber -- its resilience and elasticity -- its ability to push
tightly against a surface and conform to its contour, thus preventing
the flow of fluid through the interface, are the characteristics of
utility. High frictional properties here are valueless and usually
detrimental. No one wants an O-ring to wear out, and no one wants
a hatch seal to stick. Yet in every ship, submarine, airplane, tank,
truck, automobile, or other engine-powered device produced to date
we have built in the seeds of rapid wear, failure, and high mainten-
ance costs when we have used elastomeric materials with high fric-
tional surface properties in applications where elasticity and resil-
ience are the properties of value and interest.

Obviously, there is a clear-cut need for being able to use
elastomers for sealing purposes without making concessions to dam-
aging friction. To do that, we must know something about friction
as it pertains to elastomers.

Knowing something about friction is not easy. The deeper
you get into the subject, the more you find how little you know.
Simply, friction is the resistance to relative motion of two bodies
in contact. It can vary from frustrating resistance to a theoretical
zero. The application of a lubricant at the interface diminishes the
frustration. Obviously, a "no-friction" condition would be ideal in
certain applications for elastomers, but this one hardly hopes to
attain.

When a frictional condition exists between an elastomer and
an unyielding surface, another effect enters the picture. The ap-
plied force first deforms the elastomer. Then, a "breakaway" occurs
after the elastic resistance of the body to motion has been overcome.
Our knowledge of this phenomenon is hazy, and the nomenclature used
in connection with it is confused, but, rightly or wrongly, we call
it "stick-slip" or "breakaway". Without going any further into the
physics of it, I believe you can see that it is a factor that enters
into whether or not the hatch door opens easily or sticks. High
breakaway forces serve no good where rubber is used for seals; some-
times they become so great that the seal is torn loose from its
mounting, as we all know from our experience with automobile door
seals.

The coefficient of friction (C_f) is usually mathematically
defined as the ratio of the tangential force (F) needed to move the
normal load (N):

$$C_f = \frac{F}{N}$$

Such variables as the intensity of the load, deformation of the con-
tact area, time of contact, the velocity and length of slide, tem-
perature, sliding surface condition, and others affect the value.
These parameters have so great a total effect on C_f values that,
generally speaking, only relative performance characteristics can be

reported for the best possible set of standard conditions.

The friction we observe and try to define is, of course, a macrophenomenon. Obviously, it must arise from certain microcharacteristics of the sliding surfaces, and these could be either physical or chemical. The reasons for the existence of friction is a complex subject on which many volumes have been written, but in respect to elastomers, it has been shown quite clearly that surface free energies play a significant role. A leading and frequently quoted researcher in this area is Dr. W. A. Zisman, of the Naval Research Laboratory, who has demonstrated that materials with low surface free energies are materials that exhibit low coefficients of friction. This being the case, one has a logical approach for diminishing the high frictional characteristics of rubber -- namely, develop a method to reduce surface free energies.

Quantum's slippery rubber process is just that -- a treatment that reduces the surface free energy of a hydrocarbon elastomer. This is accomplished by converting some of the CH groups in the molecules near the surface into CF groups. The dipole forces associated with CH groups are high, while those associated with CF groups are low. Consequently, through this conversion, the surface frictional qualities of the elastomers are changed from high to low, or, as we say, lubricity is imparted. The elastomer in effect achieves a Teflon-like surface, or becomes "greasy" to the feel. The "rub" is gone from the rubber, yet the elasticity and other bulk characteristics remain essentially unchanged.

This change of surface CH groups into CF groups can be accomplished in several ways -- all involving graft polymerization. In a typical conversion, methyl acrylate is grafted onto the ultra-violet-activated surface of natural rubber. It is then hydrolyzed, and subsequently fluorinated with sulfur tetrafluoride. The exact graft polymerization procedure used depends on the elastomer being treated and other considerations associated with size and shape of the finished product and manufacturing requirements. The chemistry is conventional graft polymerization chemistry; only the adoption and adaptation of this chemistry to effect a radical change in the surface properties of elastomeric materials are new.

The first question everyone asks is: "But will it wear?" Offhand, it would seem that a thin film might wear off so rapidly that little practical benefit would result. And it is obvious that the film must be kept very thin; otherwise, bulk properties would be seriously affected.

At first we thought that film thicknesses would have to be of the order of ten to fifteen mils to provide adequate wear resistance for practical purposes. But wear tests soon established that films from two to five mils thick are adequate. Various rubber stocks given the treatment have held up as long as one thousand hours

in wear tests at a lineal speed of 114 inches per second and a pressure of 1.0 psi. The tests were made with rotating cylinders and fixed samples. Wearing to destruction of lubricity has been so time consuming that we have established two hundred hours as a standard test time.

Figure 1 shows typical changes in the coefficient of friction with time at a test speed greater than one hundred inches per second under a 1.0 psi load. You will note that the coefficient of friction at first drops rapidly and then continues to drop slowly up to 150 hours. This means, for a while, at least, slippery rubber gets more slippery as you use it -- a desirable state of affairs.
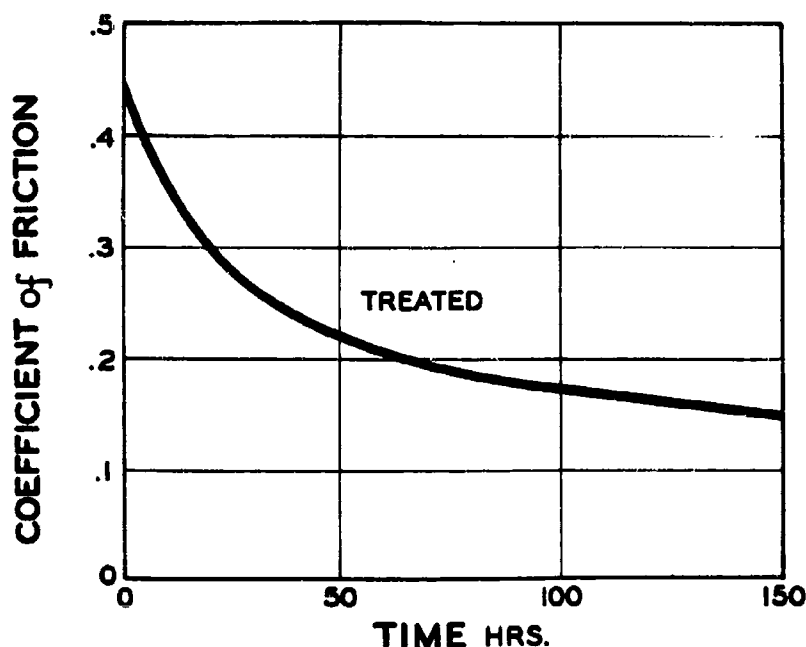
Figure 1

Change in Coefficient of Friction with Time

(Speed > 100/in/sec. -- load 1.0 psi)

One explanation for this is as follows: the fresh sample at the microscopic and submicroscopic levels would have a surface made up of ridges and valleys. These ridges and valleys would lock with similar asperities in the contacting surface, thus creating a physical type of resistance. Once worn smooth or "smeared out", this

physical resistance would tend to disappear.

Another factor is undoubtedly the filling of valleys in the contacting surface with particles of fluorocarbon torn from the treated polymer. This means that not only is physical resistance decreased, but that more of the sliding is taking place between films having low surface free energies.

Figure 2 shows the starting coefficient of friction of untreated and treated rubber with increasing load. Note that with slippery rubber the starting coefficient remains essentially constant under increased load, and it is considerably less than for untreated material. This is the stick-slip or breakaway phenomenon we mentioned earlier. The treatment gives rubber stick-slip characteristics essentially the same as those of Teflon. This is true for all base polymers treated by the process.
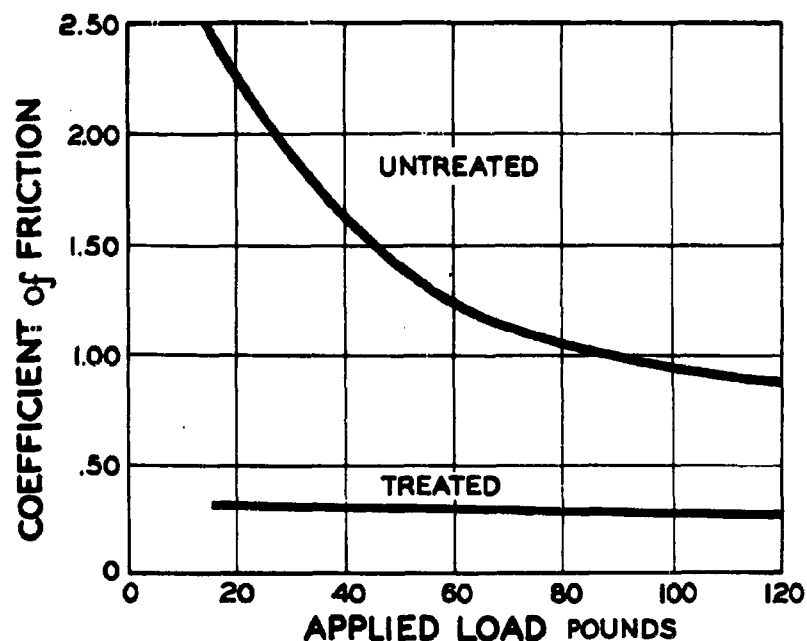
Figure 2

Starting Coefficient of Friction vs. Load[1]

Figure 3 shows coefficient of friction with speed of slide and Figure 4, with temperature rise. The shapes of these curves are as expected.
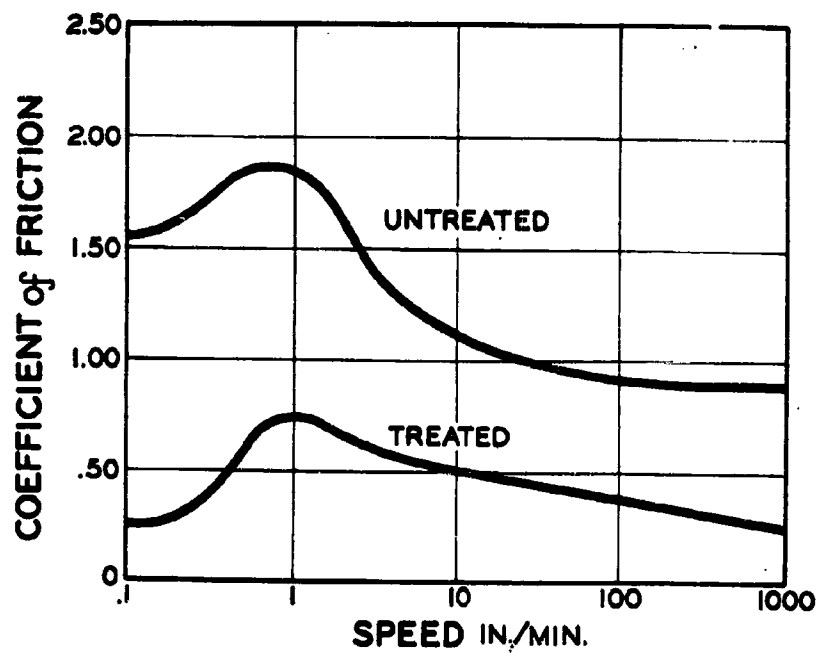
Figure 3

Coefficient of Friction vs. Speed
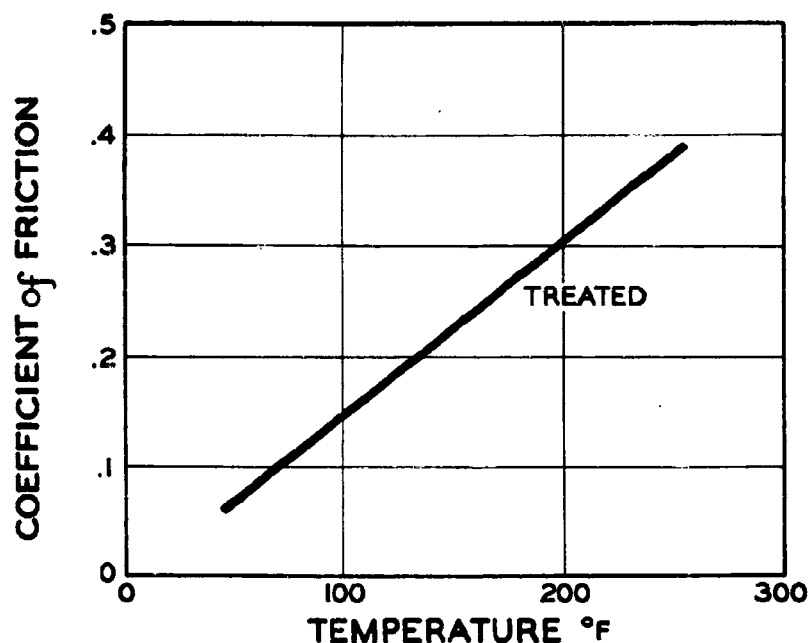
Figure 4

Coefficient of Friction vs. Temperature

The data presented so far have dealt with the desirable
frictional changes induced by the treatment. But how about the ef-
fects on other properties -- the ones we wish to retain in slippery
rubber?

Table 1, indicating changes in modulus, elongation, tensile
and hardness, shcws the types of changes that have been encountered
in treating Neoprene, Buna N, natural, and SBR rubbers.

159

Table 1

ELASTOMER	MODULUS			ELONG.	TENSILE	HARDNESS
	100%	200%	300%	(%)	(psi)	Shore A
Neoprene						
Untreated	485	1230		250	1630	60
Treated	750	1330		190	1340	69
Buna N						
Untreated	150	240	380	700	1200	47
Treated	150	260	410	540	720	44
Natural						
Untreated	300	830	1540	520	3400	57
Treated	440	1050	2040	430	2310	62
SBR						
Untreated	280	730	1480	470	2870	60
Treated	360	850	1550	420	2290	65

These changes, for the most part, are minor and unlikely to be detrimental in intended applications. They are probably brought about by at least two factors: a post cure resulting from the thermal cycle of the process, and a possible additional vulcanization caused by the introduction of small amounts of sulfur by certain of the chemical reagents. In the research we have been using commercial rubber formulations. When O-rings and seals are being manufactured to receive the slippery rubber treatment, one would, of course, use formulations designed to give the specified properties after the graft polymerization treatment. Thus, a formulation would be used that would give a five to ten points lower durometer than is desired in the finished part to prevent any deleterious effects by the slight post cure hardening. Similarly, the activators, accelerators, and antioxidants used would be those less likely to produce problems during the graft polymerization treatment.

A more serious problem is that some thin sheet stocks may become crazed and sharp edges may lose flexibility. We feel, however, that practically all deleterious effects can be overcome by modification of the process to suit the product or by readjustment of the recipe from which the part has been formulated. In some cases, minor changes in the design of the rubber product may circumvent treatment difficulties; thus, a round edge might be substituted for a sharp edge, where the latter serves no utility, to avoid a loss of flexibility.

The potential applications for slippery rubber in marine,

aircraft, space, and vehicular products are believed to be numerous. The same applies to building products and many consumer items. In general, slippery rubber may be advantageous wherever a metallic or other hard surface makes pressure contact with an elastomer under either static or dynamic conditions. Under static conditions, nonstick benefits would be obtained; under dynamic conditions, friction and heat buildup would be reduced and the life and serviceability of the rubber part increased. A long list of potential applications would include O-rings, lip seals, hatch seals, periscope seals, window channel guides, nonstick gaskets, bulging rubbers, diaphragms, rollers, windshield wiper blades, door seals, cup seals, V-packings, carrier belting, extrusions, valve packings, weatherstripping, rocket launching seals, butterfly valve packings, bearings, metal-backed pressure flanges, universal joint enclosures, and others. Some of these applications are now being field tested in the Bureau of Ships' program.

At Quantum, we regard the current effort as the forerunner of a whole series of new materials that will be created through surface modification. It is apparent that graft polymerization can also be used to modify the surfaces of elastomers so they are hydrophilic, hydrophobic, oleophilic, oleophobic, electrically conductive, adhesive, et cetera. Also, graft polymerization can be used to produce desirable changes in the surface properties of rigid polymers.

We believe that the Bureau of Ships' program will not only be responsible for the creation of elastomer materials having superior properties for certain applications, but will open up new paths to the tailoring of materials for specific service functions. As we all know, the big cry today is for materials that will give designers more flexibility. For too long have we been making concessions to materials inadequacies.

Slippery rubber -- and the group of new materials that the graft polymerization technique will spawn -- are steps toward materials tailored for specific engineering functions.

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(1) Development of Self-lubricating and Non-adhering Elastomeric Materials, 31 July 1961, United States Rubber Co., Naugatuck Chemical Div., Bu Nav Wep Contract NOw-60-0123-C

ANTIRADS AND PRORADS FOR DIENE RUBBERS

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INTRODUCTION

The availability and proposed applications of nuclear reactors and other sources of high energy radiation have created demands for radiation resistant elastomers and also economical processes for utilizing beneficial radiation induced reactions occurring in polymeric materials.

It is, then, desirable to know the radiation stability of each of the various types of rubbers which may find applications in nuclear environments. It is also of economic importance in certain cases to know whether radiation effects can be retarded or accelerated by certain additives referred to as "antirads" or "prorads" respectively. The extensive research conducted in these areas has recently been reviewed by Gehman and Gregson.[1] The present investigation has been concerned with the antirad and prorad activity of a variety of additives in butadiene/acrylonitrile (NBR) and butadiene/styrene (SBR) elastomers, respectively.

ANTIRADS

NBR with its excellent oil resistance and good physical properties should find wide application in such items as O-rings, gaskets and hoses in systems which must function in a nuclear environment. In general, the radiation stability of NBR is about average in comparison with other elastomers. Crosslinking and chain scission have both been observed at low and intermediate exposure doses, but at higher doses crosslinking predominates.[2]

Various factors have been observed to affect the radiation stability of NBR. The more important are: type of filler; state and type of cure; acrylonitrile content and the presence of antirads.

In general, filler loaded elastomers are more radiation resistant than pure gum stocks. Of the fillers, carbon black appears to be the best for improving the radiation stability of elastomeric compounds.[2]

The state of cure of the vulcanizate is also important. An undercure is to be preferred as the onset of degradation by high energy radiation is, thereby, delayed until the radiation completes the cure.[3,4]

Sulfur cured NBR has been demonstrated to have more radiation stability than peroxide and radiation cured materials at acrylonitrile concentrations of less than 33%. The 20% acrylonitrile rubber has been found to be the most stable of the sulfur cured vulcanizates and the most suitable for applications requiring minimum change in strength properties when irradiated.[5] In general, it appears that increasing the acrylonitrile content of NBR produces only a slight improvement in its radiation stability.[3]

In lieu of the development of inherently radiation stable elastomers with desired physical and chemical properties, the most promising approach to radiation resistant elastomers appears to be by the incorporation of suitable antirads. Several additives when present in low concentrations have been found to impart moderate improvement in the radiation resistance of the more common elastomers.[3,6-13]

According to Charlesby,[14] antirads may act to protect a polymer from radiation by: removing the absorbed energy before chemical changes occur; inactivating radicals on the polymer formed by radiation and protection of a polymer against reactive entities produced elsewhere in the system.

In this investigation, approximately 200 potential antirads have been evaluated in a screening program to determine the best antirads for low acrylonitrile content NBR. The standard recipe for the vulcanizates used in this study is as follows: (See Appendix I for all other recipes.)

	Pts. by Wt.
NBR (78/18 butadiene/acrylonitrile)	100
Stearic acid	1
Zinc oxide	5
Polymerized trimethyldihydroquinoline	1
Benzothiazyl disulfide	1.5
Sulfur	1.5
SRF carbon black	60
Potential antirad	5
Cure: 30 minutes at 153°C.	

All vulcanizates were compounded, milled, cured and tested in accordance with conventional ASTM procedures.[15] Specimens were

163

cut, wrapped in aluminum foil, placed in a confined enclosure and irradiated in a water and concrete shielded Co^{60} source at a dose rate of approximately 2.5×10^5 rads/hour. After irradiation, all specimens were tested and compared with appropriate controls. (A complete list of all potential antirads evaluated can be obtained by referring to Ref. No. 9 and Appendix II.) Those compounds whose vulcanizates met the following requirements after receiving a dose of 50 megarads were judged to possess significant antirad activity: NBS strain 50%, % of initial value $>$ 50%; ultimate elongation 200%, % of initial value $>$ 50%; and ultimate tensile $>$ 2000 psi.

Based on these requirements, the 12 best antirads evaluated are given in Table I where they are arranged in descending order according to their antirad activity. Activity was judged by the percent of initial NBS strain and Shore A hardness values respectively after a dose of 50 megarads. (Actual values of these properties are given in Appendix III.) From Table I, it can be seen that several aromatic nitro compounds function as inhibitors of radiation damage in this type of rubber. In particular, 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 1,1-diphenyl-2-picrylhydrazine (DPPH$_2$) appear to be the most efficient antirads. The mechanism of their protective action can probably be attributed to their function as radiation stabilized scavengers for free radicals produced by high energy radiation.

TABLE I

EVALUATION OF THE BEST ANTIRADS IN NBR

Additive (5 pph Polymer)	Percent of Original Property after 5×10^7 Rads			
	Ten-sile	Elong-ation	Hardness Shore A	Strain NBS
None (Control)	92	33	116	34
2,2-Diphenyl-1-picrylhydrazyl	109	61	104	58
1,1-Diphenyl-2-picrylhydrazine	98	63	108	55
N,N'-Diphenyl paraphenylenediamine	82	51	110	55
1-Fluoro-2,4-dinitrobenzene	113	70	116	55
5-Nitro-1-naphthylamine	100	58	110	54
p-Phenylazoaniline	95	53	114	54
4-Phenylazodiphenylamine	91	51	112	53
2-Nitrodiphenylamine	97	51	112	52
Phenothiazine	93	51	115	52
p-Nitrobenzonitrile	97	52	118	52
p-Nitrobenzhydrazide	92	51	112	51
p-Nitrophenylhydrazine	113	60	113	50

It is not known exactly how DPPH and DPPH$_2$ may attach to the free radicals produced in the NBR vulcanizate. Overall, [16]

for example, has concluded from electron paramagnetic resonance spectra of polymethyl methacrylate prepared by the free radical polymerization of the monomer in the presence of $DPPH_2$, that the polymers contain $DPPH_2$ end groups. These groups can be oxidized to DPPH indicating the addition of polymethyl methacrylate propagating radicals to the aromatic rings of $DPPH_2$ rather than addition to the nitrogen atom. Polystyrene prepared in the same manner, however, gave evidence that addition occurs at the nitrogen atom.

In the case of NBR, then, DPPH and $DPPH_2$ may possibly add to free radicals produced during curing or irradiation in either manner, thereby, enhancing the radiation stability of the vulcanizate.

The antirad activity of $DPPH_2$ present at a concentration of 5 pph polymer was also investigated in SBR, butyl and natural rubber. A significant antirad activity is exhibited in only the SBR vulcanizate as can be seen from Table II.

TABLE II

EVALUATION OF $DPPH_2$ IN VARIOUS ELASTOMERS

Polymer	Additive	Percent of Original Property after 5×10^7 Rads			
		Tensile	Elongation	Hardness Shore A	Strain NBS
SBR	None	98	55	117	51
"	$DPPH_2$	112	84	108	65
Butyl	None	4	71	59	-
"	$DPPH_2$	4	70	66	-
Natural	None	86	67	112	64
"	$DPPH_2$	80	71	106	78

Shelberg,[8] subsequently, reported the inactivity of DPPH as an antirad in natural rubber vulcanizates. Turner,[11] however, using purified pale crepe found that DPPH did possess significant antirad activity in samples which had been rigorously outgassed.

The effectiveness of one of the best antirad systems for NBR is presented in Figures 1, 2, & 3 where the effect of gamma radiation on the ultimate tensile, elongation and Shore A hardness is illustrated. In each of these figures the corresponding data for unprotected NBR and natural rubber are included to illustrate the degree of protection obtained with a suitable antirad. The presence of both $DPPH_2$ and N,N'-di-3(5 methyl heptyl)-p-phenylenediamine each at a concentration of 5 pph polymer appears to afford only slightly
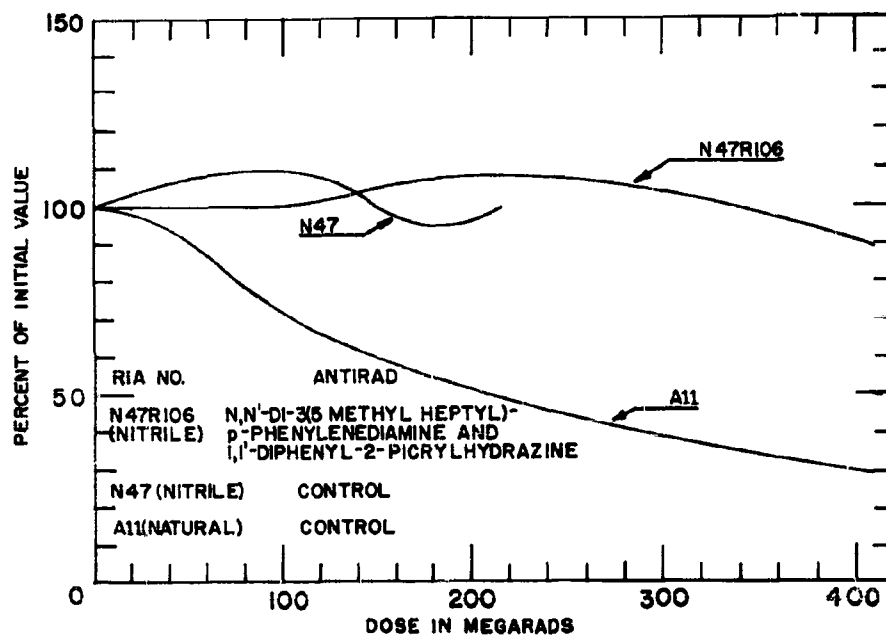
FIG. 1 — THE EFFECT OF GAMMA RADIATION ON THE ULTIMATE TENSILE STRENGTH
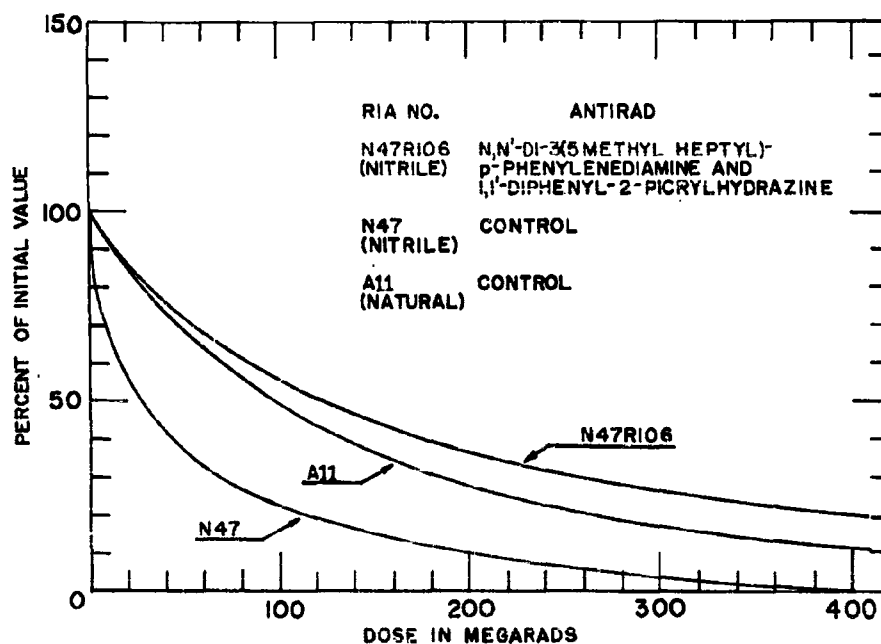
FIG. 2 — THE EFFECT OF GAMMA RADIATION ON THE ULTIMATE ELONGATION

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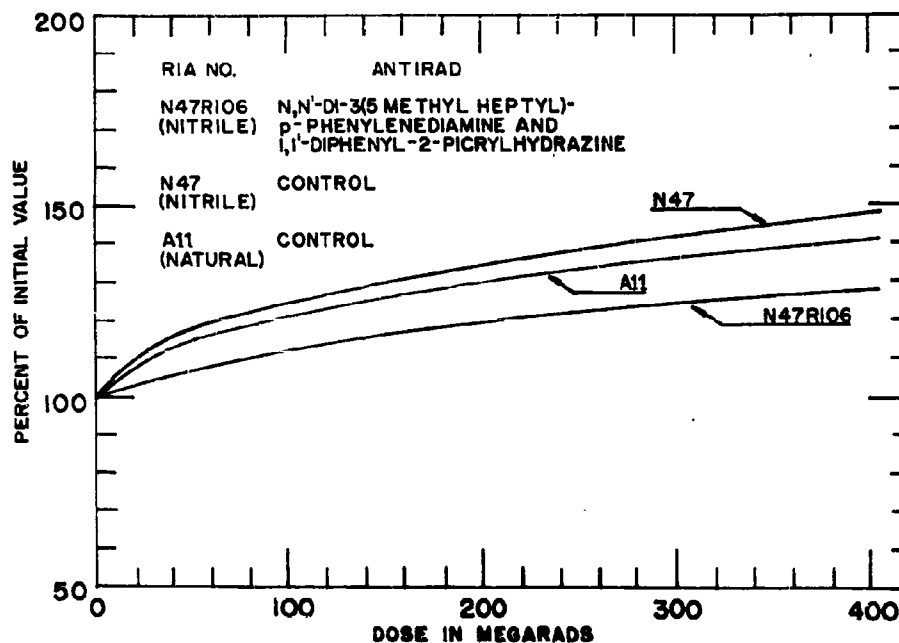
FIG. 3 - THE EFFECT OF GAMMA RADIATION ON THE SHORE A HARDNESS
3906

better protection than 10 pph of DPPH$_2$ alone and significantly
better protection than 10 pph of N,N'-di-3(5 methyl heptyl)-p-
phenylenediamine.   (See Appendix III.)

These results, then, indicate that a good antirad system will
impart a degree of protection to NBR approaching or surpassing that
which is inherent in natural rubber.   It is also indicated that an
effective antirad will usually possess one or all of the following
characteristics; antioxidant or antiozonant activity; aromaticity;
be an efficient radical acceptor; and contain aromatic nitro group(s).

PRORADS

In addition to the search for antirads for diene rubbers, there
is also a practical interest in finding additives or prorads which
will enhance the crosslinking efficiency of high energy radiation,
thereby, making radiation vulcanization economically feasible for
rubbers such as SBR which normally require from 30 - 50 megarads to
produce acceptable radiation vulcanizates.   The radiation vulcaniza-
tion of a variety of elastomers has been reported and it has been
found that nearly all commercial elastomers except butyl rubber can
be vulcanized even though they possess very different structures.[17-
40)

Harmon[37] has determined for natural, SBR, nitrile, neoprene and fluorinated elastomers that radiation cures provide lower tensile strength and ultimate elongation than chemical cures, but abrasion resistance is usually higher. Other properties such as permanent set, hardness, resilience, ozone cracking and solvent resistance are about equal for the two curing methods. It has also been demonstrated by both Harmon[37] and Ossefort[38] that radiation cured SBR vulcanizates containing an antioxidant, exhibit improved retention of tensile strength and breaking elongation after aging at elevated temperatures and are superior to a conventional chemical vulcanizate in these respects.

Several investigators have also found that certain additives have a pronounced accelerating effect on the radiation vulcanization of various rubbers. These studies have shown that halogenated derivatives, [11, 25, 41] metallic oxides,[42] vinyl monomers,[42-44] divinyl monomers,[45] di and triallyl esters [46, 47] and dimaleimides[48] act as chemical sensitizers or prorads which enhance radiation vulcanization.

In the present screening study, the prorad activity of several halogenated derivatives and various monomers has been evaluated at a concentration of 5 pph polymer in unextracted, filler loaded SBR 1500 after a dose of 22.5 megarads. The ability of these potential prorads to enhance the radiation vulcanization of this general purpose rubber has been evaluated by comparing the physical properties and the number of moles of effective network chains per gram of their vulcanizates with suitable controls.

The standard recipe for radiation cured specimens was: (See Appendix I for control recipe.)

	Pts. by Wt.
SBR 1500 (76.5/23.5 butadiene/styrene)	100
Stearic Acid	2
Polymerized trimethyldihydroquinoline	1
Phenyl beta naphthylamine	1
FEF Carbon black	50
Potential prorad	5

Specimens for radiation curing were compounded on a conventional 2 roll mill, and cold pressed between sheets of aluminum foil to a thickness of approximately 0.1 in. in a conventional ASTM test pad mold. The foil served to exclude oxygen and prevent the diffussion of the more volatile additives during irradiation in the Co^{60} source. After irradiation, physical properties were obtained and the concentration of crosslinks determined by swelling measurements.

Specimens for swelling experiments weighing approximately 1 gram were cut from the test pads, weighed and swollen in 150 ml of benzene for 3 days after which the solvent was renewed and swelling continued

for an additional 3 days. The swollen specimens were then removed from the solvent, blotted dry and reweighed in a ground glass stoppered vial. They were then placed in a vacuum oven overnight at 60°C to remove the solvent and subsequently reweighed. The number of moles of effectiv e network chains (between crosslinks) per gram, ν_e, and consequently the number of effective crosslinks in moles per gram, $\nu_e/2$, was then calculated from Flory's[49-51] expression relating swelling to the degree of crosslinking:

$$-\left[\ln(1-v_r)+v_r+\chi v_r^2\right] = (V \, \tilde{\nu}/\tilde{v}) \, (v_r^{1/3}-v_r/2)$$

where

$\tilde{v}$ = Specific volume of the polymer. (d = 0.94g/cc)
V = Molar volume of the solvent. (88.86)
v_r = Polymer volume fraction of swollen gel. (See Appendix IV)
χ = Polymer-solvent interaction parameter. (See Appendix IV)

A total of 35 potential prorads have been evaluated in SBR 1500. The eight best prorads found are given in Table III where they are arranged in descending order according to their activity factor. (A complete list of all potential prorads evaluated, the physical properties of their vulcanizates, and their activity factors is given in Appendix V.) The activity factor is simply the ratio of ν_e of a specimen containing a potential prorad to the ν_e of a control after irradiation. An activity factor of 1, then, is indicative of no prorad or antirad activity. Values greater than 1 signify prorad activity and values less than 1 indicate antirad activity.

TABLE III

ACTIVITY OF THE BEST PRORADS IN SBR 1500

Additive (5 pph Polymer)	$\dfrac{\nu_e \text{ (Prorad)}}{\nu_e \text{ (Control)}}$
No prorad or antirad activity	1.00
Acrylic acid	4.42
Carbon tetrachloride	3.39
o-Dichlorobenzene	3.36
m-Dichlorobenzene	3.12
Chloroform	2.98
Methylacrylate	2.97
p-Dichlorobenzene	2.97
Hexachloroethane	2.72

The doses required for specimens containing carbon tetrachloride
and acrylic acid to achieve crosslink concentrations equivalent to
a chemically cured vulcanizate assumed to posses an optimum cure can
be obtained from Figure IV. From the results plotted in this figure,
it can be seen that an SBR specimen containing no additive requires
a dose of 45 megarads to reach a state of cure equivalent to the
chemically cured vulcanizate. The incorporation of carbon tetra-
chloride at a concentration of 5 pph polymer reduces the required
dose to 17.5 megarads. Acrylic acid present at the same concentra-
tion, however, is much more active as it reduces the dose to only 4
megarads. The physical properties of these vulcanizates (given in
Appendix VI) appear to be equivalent to those of a non-accelerated
radiation cured vulcanizate.
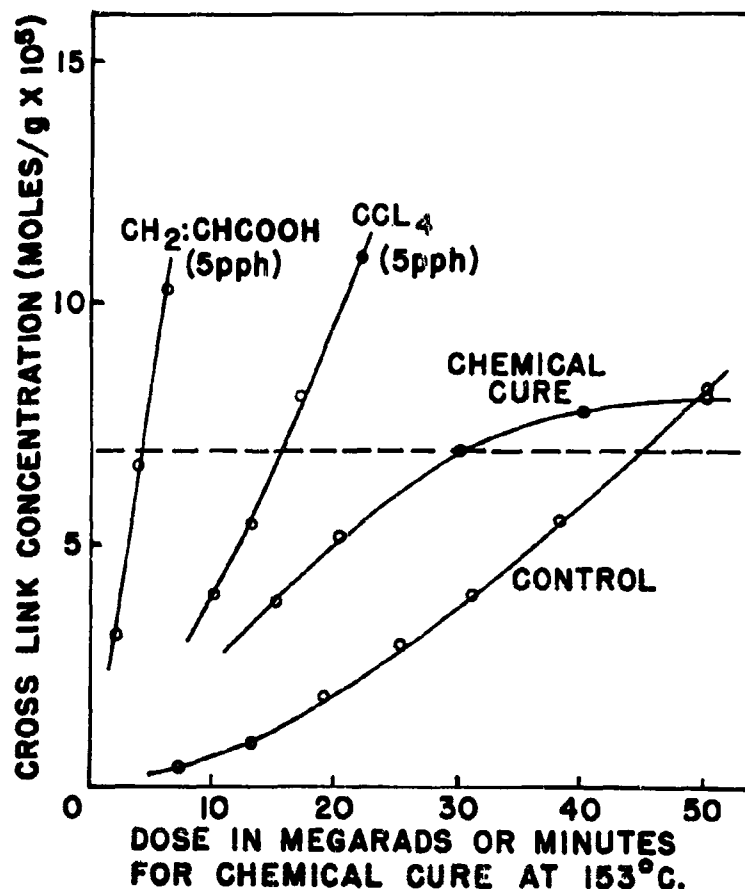
FIGURE 4. PRORAD ACTIVITY IN SBR 1500

3914

The prorad activity of halogen compounds is usually attributed to their high G values.* The action of acrylic acid as a prorad is probably similar to that described for p-chlorostyrene by Mesrobian.[44] He attributed its action to the increased average lifetimes of radicals in the rubber system by chain transfer to monomer and subsequent interaction of growing chains with segments of the rubber molecule.

As this was a preliminary screening study, no attempt was made to purify any of the materials or to remove inhibitors when present. It would be reasonable to expect even greater prorad activity for these additives if highly purified materials were utilized.

SUMMARY

In summation, then, it has been shown that several aromatic nitro compounds function as efficient inhibitors of radiation damage in nitrile rubber. In particular, 2,2-diphenyl-1-picrylhydrazyl and 1,1-diphenyl-2-picrylhydrazine appear to be the most efficient antirads probably functioning as radiation stabilized scavengers for deleterious free radicals produced by high energy radiation.

Certain organic compounds were also observed to accelerate the radiation vulcanization of SBR. Of the compounds evaluated, acrylic acid affords the most enhancement.

*The number of chemical changes of a given kind produced per 100 eV absorbed.

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171

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APPENDIX I
COMPOUND FORMULATIONS

Parts by Weight

Ingredients	Antirad Evaluation							Prorad Evaluation	
	1	2	3	4	5	6	7	Control	Rad Cure
NBR (78/18 butadiene/acrylonitrile)	100								
Pale crepe		100							
Isobutylene/isoprene			100						
SBR 1500 (76.5/23.5 butadiene/styrene)							100	100	100
Stearic acid	1	2	1				2	2	2
Zinc oxide	5	3	5				3	3	
Polymerized trimethyldihydroquinoline	1	1	1				1	1	1
Benzothiazyl disulfide	1.5								
Sulfur	1.5	1.75	1.5				1.75	1.75	
SRF Carbon black	60								
FEF Carbon black		50					50	50	50
EPC Carbon black			40						
Phenyl beta naphthylamine		1					1	1	1
N-Cylcohexyl-2-benzothiazol sulfenamide		1	1				1	1	
Tetramethyl thiuram disulfide			1						
Antirad (Usual concentration)	5	5	5				5		
Prorad (Usual concentration)									5
	Cure 30 Min at 153°C	Cure 30 Min at 153°C	Cure 30 Min at 153°C	Cure 30 Min. at 153°C	Press Cure 20 Min at 153°C Oven Cure 24 hrs at 153°C	Cure 30 Min at 153°C	Cure 30 Min at 153°C	Cure Various times at 153°C	Cure Gamma Radiation

APPENDIX II

Antirads Evaluated in Nitrile Rubber During
Second Part of Screening Program (See Ref. 9
for those evaluated in first part.)

Acridine
Aluminum dioctyldithiocarbamate
5-Amino-2,3-dihydro-1,4-phthalazinedione
p-Benzoquinone
Benzylamine
Bibenzyl
Bis(2,4-dinitrophenyl)disulfide
Bis(2,4-dinitrophenyl) methane
Bis (p-nitrophenyl) disulfide
1,4-Bis (2-(5 phenyloxazolyl))-benzene
Boric acid
2,3-Butanedione oxime-2,4-dinitrophenylhydrazone
Carbazole
Diallyl aniline
Dibenzylamine
Dilaurylthiodipropionate
Dinaphthylenethiophene
Dibetanaphthyl-p-phenylenediamine
2,4-Dinitroaniline
2,4'-Dinitrobiphenyl
4,4'-Dinitrobiphenyl
2,4'-Dinitrodiphenylamine
2,4-Dinitrophenylhydrazone of formyl ferrocene
N,4-Dinitroso-N-methylaniline
1,4-Dinitrosopiperzine
2,5-Diphenyloxazole
N,N'-Diphenyl-p-phenylenediamine
Durene
EDTA, tetra sodium salt
(Ethylenedinitrilo) tetra acedic acid tetra sodium salt
Fluorobenzene
p-Fluorobenzonitrile
1-Fluoro-2,4-dinitrobenzene
1-Fluoro-4-nitrobenzene
p-Fluorotoluene
Galvinoxyl
Hexabromobenzene
Hydrazobenzene
2(2'-Hydroxy-5'-methylphenyl) benzotriazole
Iodine
4,4'-Methylenebis(2,6-di-tert-butylphenol)
1-Naphthylamine
2,2',2''-Nitrilotriethanol
p-Nitrobenzenediaozonium fluoborate
p-Nitrobenzyhydrazide

176

APPENDIX II (CONT.)

5-Nitro-2-benzimidazolethiol
p-Nitrobenzonitrile
2-Nitrodiphenylamine
2-Nitrofluorene
5-Nitroindazole
Nitromesitylene
Nitron
1-Nitronaphthalene
5-Nitro-1-naphthylamine
4-Nitro-o-phenylenediamine
3-(p-Nitrophenyl)-1-(p-phenylazophenyl) triazene
N-Nitrosodiphenylamine
p-Nitrosodiphenylamine
Octylated diphenylamines
Phenanthrene
Phenathiazine
p-Phenylazoaniline
4-Phenylazodiphenylamine
p-Phenylenediamine
Phenyl-beta-naphthylamine
65%N-Phenyl-beta-naphthylamine + 35% N,N'-diphenyl-p-phenylenediamine
Potassium permanganate
Pyrogallol
o-Terphenyl
Tribenzylamine
Triphenylamine
Triphenylgnanidine
Tris(2-biphenyl) phosphate
Quinhydrone
Quinizarin
Quinoline

Polymer	Antirad (pph Polymer in Parenthesis)	Dose Rads X10⁶	Tensile		200% Mod.		Elongation		Hardness		Strain at 400 psi	
			psi	% of Orig.	psi	% of Orig.	%	% of Orig.	Shore A	% of Orig.	%	% of Orig.
Nitrile	None – Typical control	0	2420		688		445		62		135	
		50	2220	92	-	-	145	33	72	116	46	34
Nitrile	(5) 2,2-Diphenyl-1-picrylhydrazyl	0	2510		910		415		67		115	
		50	2740	109	2310	254	255	61	70	104	67	58
Nitrile	(5) 1,1-Diphenyl-2-picrylhydrazine	0	2530		790		415		65		127	
		50	2470	98	1870	237	260	63	71	108	70	55
Nitrile	(5) N,N'-Diphenyl paraphenylene diamine	0	2470		722		475		61		139	
		50	2020	82	1610	223	240	51	67	110	77	55
Nitrile	(5) 1-Fluoro-2,4-dinitrobenzene	0	2260		880		385		62		123	
		50	2550	113	2010	228	270	70	72	116	68	55
Nitrile	(5) 5-Nitro-1-naphthylamine	0	2230		590		515		60		154	
		50	2230	100	1440	244	300	58	66	110	83	54
Nitrile	(5) p-Phenylazuaniline	0	2400		640		500		59		152	
		50	2270	95	1720	264	265	53	67	114	82	54
Nitrile	(5) 4-Phenylazodiphenylamine	0	2390		600		485		60		150	
		50	2180	91	1670	278	245	51	67	112	80	53
Nitrile	(5) 2-Nitrodiphenylamine	0	2430		640		530		60		153	
		50	2350	97	1490	233	270	51	67	112	73	52
Nitrile	(5) Phenothiazine	0	2310		670		470		59		149	
		50	2150	93	1770	264	240	51	68	115	78	52
Nitrile	(5) p-Nitrobenzonitrile	0	2150		790		410		60		131	
		50	2080	97	1830	232	215	52	71	118	68	52
Nitrile	(5) p-Nitrobenzuydrazide	0	2250		810		460		65		128	
		50	2080	92	1880	232	235	51	73	112	65	51
Nitrile	(5) p-Nitrophenylhydrazine	0	2140		470		580		60		181	
		50	2420	113	1420	302	350	60	68	113	90	50
SBR	None – Control	0	2580		740		480		60		129	
		50	2530	98	1700	210	265	55	70	117	66	51
SBR	(5) 1,1-Diphenyl-2-picrylhydrazine	0	2420		970		435		60		127	
		50	2700	112	1370	141	365	84	65	108	82	65
Butyl	None – Control	0	2580		360		700		54		234	
		50	95	4	-	-	500	71	32	59	-	-
	(5) 1,1-Diphenyl-2-picrylhydrazine	0	2460		280		710		53		270	
		50	102	4	-	-	500	70	35	66	-	-
Natural	None – Control	0	2210		860		380		58		136	
		50	1890	86	1470	171	255	67	65	112	87	64
	(5) 1,1-Diphenyl-2-picrylhydrazine	0	2530		1380		340		63		91	
		50	2030	80	1740	126	240	71	67	106	76	78
Natural	None – Control	0	2370	-	670	-	420	-	58	-	122	-
		50	2160	91	1280	191	295	70	67	116	83	68
		100	1740	73	1710	255	205	49	68	117	66	54
		200	1260	53	-	-	115	27	76	131	45	37
		400	680	29	-	-	55	13	82	141	-	-
Nitrile	None – Control	0	2440	-	610	-	460	-	66	-	142	-
		50	2560	105	-	-	165	36	78	118	37	26
		100	2690	110	-	-	105	23	81	123	22	15
		200	2330	95	-	-	60	13	88	133	10	7
		400	Brittle	-	-	-	-	-	98	148	-	-
Nitrile	(5) N,N'-Di-3(5 methyl hepytl)-p-phenylenediamine + (5) 1,1-diphenyl-2-picrylhydrazine	0	2280	-	630	-	475	-	62	-	150	-
		50	2280	100	1240	197	335	71	66	107	97	65
		100	2270	100	1740	276	260	55	67	108	76	51
		200	2460	108	2460	390	200	42	63	118	52	35
		400	2070	91	-	-	90	19	80	129	25	12
Nitrile	(10) 1,1-Diphenyl-2-picrylhydrazine	0	2540	-	760	-	465	-	62	-	134	-
		50	2500	98	1470	193	310	67	67	108	85	63
		100	2730	107	2110	278	245	53	70	113	66	49
Nitrile	(10) N,N'-Di-3(5 methyl hepytl)-p-phenylenediamine	0	1930	-	200	-	645	-	55	-	214	-
		50	2210	114	930	465	395	61	64	116	99	46
		100	2100	109	1460	730	275	43	67	122	74	35
		200	2120	110	-	-	195	30	73	133	55	26
		400	1610	83	-	-	85	13	82	149	25	12

5917

178

APPENDIX IV

CALCULATION OF v_r AND χ

The polymer volume fraction (v_r) was calculated as follows:

$$v_r = \frac{\text{Polymer volume}}{\text{Solvent volume} + \text{polymer volume}} =$$

$$\frac{(w_3 - w_1 a)/d_r}{(w_2 - w_3)/d_b + (w_3 - w_1 a)/d_r}$$

where

w_1 = Original specimen weight.

w_2 = Swollen specimen weight.

w_3 = Dry extracted weight.

a = Insoluble filler fraction (Control = 0.3247. Prorad samples = 0.3145).

d_r = Density of the polymer (0.94g/cm^3)

d_b = Density of benzene (0.87901g/cm^3)

The polymer-solvent interaction parameter was calculated as follows:

$$\chi = \chi_o + \beta\, v_r$$

where $\chi_o = 0.37$, and $\beta = 0.27$ as determined by Kraus[52] for SBR 1500.

APPENDIX V
EVALUATION OF POTENTIAL PRORADS IN SBR

Additive (5 pph Polymer)	Dose Rads X10^-6	Tensile psi	Mod. 300% psi	Elong. %	Hardness, Shore A	$\frac{\gamma e \text{ (Prorad)}}{\gamma e \text{ (Control)}}$
None (Typical Control)	22.5	1170	580	595	58	-
Acrylic acid	"	1650	-	240	62	4.42
Carbon tetrachloride	"	1650	1500	335	64	3.55
o-Dichlorobenzene	"	1860	1610	375	65	3.40
m-Dichlorobenzene	"	1730	1460	385	65	3.12
Chloroform	"	1600	780	355	63	2.98
Methyl acrylate	"	1530	1530	300	53	2.97
p-Dichlorobenzene	"	1860	1500	420	64	2.97
Hexachloroethane	"	1560	1320	375	62	2.72
p-Chlorostyrene	"	1420	1110	435	63	2.59
Chlorendic Anhydride	"	1380	1160	405	62	2.33
1,1,2,2-Tetrachloroethylene	"	1340	1130	385	62	2.26
Acrylonitrile	"	1350	1146	290	54	2.07
1,2-Dibromo-1,1,2,2, tetrafluoroethylene	"	1430	990	445	60	2.04
Ethyl methacrylate	"	1420	1180	390	53	1.92
t-Butylaminoethyl methacrylate	"	1740	1241	440	55	1.81
Methyl methacrylate	"	1410	1184	350	58	1.81
Allyl methacrylate	"	1510	1170	415	55	1.81
p-Dibromobenzene	"	1570	1440	370	62	1.73
Butyl methacrylate	"	1380	1045	385	53	1.70
Vinylidene chloride	"	1440	440	425	50	1.46
Divinyl benzene	"	1010	870	385	50	1.44
Chlorowax 70	"	1130	600	590	55	1.34
Polyethylene glycol dimethacrylate	"	1300	985	410	55	1.31
Hydroxypropyl methacrylate	"	1140	770	400	52	1.19
Hexabromobenzene	"	1280	640	575	57	1.19
Chlorendic acid	"	1080	580	560	57	0.95
Vinyl butyrate	"	1160	570	440	53	0.89

APPENDIX V (CONT.)

Additive 5 pph Polymer	Dose Rads $\times 10^6$	Tensile psi	Mod. 300% psi	Elong. %	Hardness, Shore A	ηe (Prerad) / ηe (Control)
Vinyl acetate	22.5	990	545	460	47	0.86
3,3',4',5,7 Pentahydroxy flavone	"	910	415	575	55	0.77
Triallyl cyanurate	"	750	645	525	45	0.69
Styrene	"	930	540	475	45	0.65
Diallyl amine	"	990	470	585	45	0.62
Boron	"	920	410	610	46	0.59
Acrolein	"	705	355	525	48	0.54
N,N-Diallyl aniline	"	630	270	660	45	0.36

APPENDIX VI
EVALUATION OF PRORAD ACTIVITY IN SBR 1500

Additive	Cure Chem. Min	Cure Rads X10^{-6}	Tensile psi	Mod. 300% psi	Elong. %	Hardness Shore A	NBS Strain at 400 psi %	$\frac{\nu_e}{2}$ X10^5 moles/gm
None - Control	15		2290	740	755	60	212	3.83
	20		2670	1110	645	61	172	5.17
	30		2870	1390	545	64	150	6.97
	40		2750	1530	495	66	139	7.74
	50		2860	1570	505	65	133	8.00
	60		2860	1480	500	66	133	7.91
None - Control		7	120	70	970	46	-	0.39
		13	530	200	690	50	463	0.90
		19	920	420	535	52	291	1.88
		25	1420	570	645	54	229	3.00
		31	1540	790	555	57	185	3.99
		38	1850	1100	500	58	161	5.52
		50	1610	1350	330	62	123	8.26
Carbon tetrachloride (5 pph polymer)		10	1610	900	535	54	-	4.00
		13	1900	1230	500	55	-	5.41
		17	1760	1500	350	58	-	8.09
		22	2230	1910	350	62	-	10.97
Acrylic acid (5 pph polymer)		2	1040	560	575	52	230	3.16
		3.7	1930	1250	460	60	131	6.62
		6	1700	1700	300	65	105	10.27

THE RELATIONSHIP BETWEEN RADIATION INDUCED COMPRESSION SET AND THE DEGREE OF VULCANIZATION IN NATURAL RUBBER

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This study deals with the effect of additives and cure on compression set, crosslinking, and chain scission in an irradiated rubber vulcanizate. It is part of a continuing investigation on the interaction of nuclear radiation with elastomeric materials.[1-4] These elastomers are of interest for their possible use as component parts of devices which may be used in prolonged or intense nuclear radiation fields on earth or in space.

It was shown previously by the authors that there is a linear relationship between radiation-induced compression set and degree of cure of a rubber cylinder:[1]

$$S = kC_o + K \tag{1}$$

where S = Percent compression set
C_o = Number of pre-irradiation crosslinks per gram
k and K = Constants for a particular energy absorbed per gram.

The earlier study was based on different degrees of cure which were the result of the additive, whereas the present study used samples of identical composition which were cured for different lengths of time. One purpose of the present study was to confirm the relationship expressed in Eq. 1.

Evaluation of an anti-rad can be made by comparing the expected value of compression set, based on the measurement of pre-irradiation crosslinks, to the experimental value. If the experimental value is significantly less than that predicted, the added compound can be considered an anti-rad. If greater, radiation sensitization can be assumed.

The present study also endeavored to evaluate as anti-rads the following types of compounds; aromatic hydrocarbons, hydrazines, phenols, quinoids, organo-metallics, mercaptans, and amines.

Previous work established a method for determining radiation yields of chain scission and crosslinking for rubber vulcanizates. This method combined set and solvent-swelling measurements, and was applied to the vulcanizates described herein.

EXPERIMENTAL

Test specimens were measured for length, and were compressed, irradiated in a nitrogen atmosphere, released, allowed to recover at $40^{\circ}C$, re-measured for compression set, and then measured for crosslinking by solvent swelling. Also, initial crosslinking (cure) was determined using similar specimens. Statistical treatment of the compression set versus initial crosslinking data established Eq. 1 as the regression line relating set and cure at a 10^8 r dose.[3]

Rubbers

All rubber specimens were cylinders cured in a mold. The dimensions of the mold forms were 0.5-in. depth and 0.425-in. diameter.

Fourteen rubber stocks of identical composition but having different states of cure were prepared by varying the cure time. The following weight recipe and a $260^{\circ}F$ cure were used; deproteinized pale crepe, 100; sulfur, 2; zinc oxide, 3; zinc dibutylidithiocarbamate, 0.25; 2-mercaptobenzothiazole, 0.4; and carbon (Thermax), 50. Table 1 shows the cure times used and the extent of crosslinking they produced.

Also, fifty-six rubber stocks of the above composition were prepared except that each contained 5 parts of a unique additive to be evaluated as an anti-rad. Cure conditions were 20 minutes at $260^{\circ}F$, but the chemical nature of the additive affected the degree of cure so that a variety of cures were obtained. Test specimens were similar in recipe, shape, and preparation to the additive rubbers evaluated for radiation resistance in the previous study.[1] The additives tested are listed in Table 2 along with 47 additives previously evaluated for anti-rad behavior[1] but re-evaluated herein because of a difference in method of calculating compression set. The latter are identified by the footnote symbol b.

TABLE 1

Pre-Irradiation Crosslinks and Compression Sets for Rubber Stocks
Without Additives, Cured for Different Times at 260°F

Stock	Cure Time (min)	Number of Pre-Irradiation Crosslinks per gram, C_o[a] $(\times 10^{-18})$	Blank Factor F[b]	Compression Set[a]
1	6.5	7.8	0.917	90.3
2	7	8.1	0.933	90.55
3	7.5	8.5	0.933	90.8
4	8	9.5	0.945	90.2
5	8.5	10.3	0.945	87.0
6	9	10.7	0.959	85.2
7	9.5	14.8	0.968	81.7
8	10	20.3	0.987	82.4
9	15	23.0	0.991	81.6
10	20	23.5	0.995	81.7
11	20	19.3	0.996	80.5
12	25	23.2	0.996	81.0
13	30	22.7	0.996	77.7
14	35	22.6	0.996	77.5

a. Crosslinking and compression set values are averages from quintuplicate experiments.
b. Blank factors are averages from triplicate experiments.

Compression and Irradiation

Specimens were measured and compressed to 0.375 in. in compression jigs, as previously described.[1] This was done in a nitrogen-filled glove box so that the specimens were sealed within their spacers in a nitrogen atmosphere. Irradiations to 10^7 or 10^8 r were performed with a cobalt-60 source which provided 10^8 r in 530 hrs. Dosimetry was done with the Fricke ferrous sulfate dosimeter.[5] After irradiation, specimens were released from compression and allowed to recover for 3 weeks at 40°C before set length was measured. Control specimens of each stock were treated exactly as test specimens, except that they were not irradiated. The set lengths of the controls were used to calculate blank factors, F (see section headed "Compression Set"), which were used in the calculation of compression sets of test specimens.

Compression set and crosslinking data determined for vulcanizates in the previous study were re-evaluated. These vulcanizates were irradiated with gamma radiation from reactor spent fuel elements.

Crosslinking and Radiation Yields

The number of crosslinks per gram of specimens (crosslinking density) was determined by the solvent-swelling procedure of the previous experiment.[1] Pre-irradiation and post-irradiation crosslinking densities are denoted by C_0 and C, respectively. Also determined by those procedures were the number of vulcanization crosslinks per gram of specimen remaining after irradiation, C_v; the number of vulcanization crosslinks scissioned per gram of specimen due to irradiation, ΔC_0; the number of crosslinks engendered per gram of specimen in the compressed state by irradiation, C_r; and radiation yields of chain scission and crosslinking for the dose region from 0 to 10^7 r. The method for determining radiation yields combines set and solvent-swelling measurements.

Compression Set

Compression set for a test specimen is defined by Eq. 2.

$$\text{Compression set (\%)} = \frac{(\ell_0 F - \ell_s)\ 100}{\ell_0 F - \ell_c} \qquad (2)$$

where ℓ_0 = Test specimen length before compression.

ℓ_s = Test specimen length after irradiation, release from compression, and recovery.

ℓ_c = Test specimen when compressed.

F = Control, or blank factor.

TABLE 2

Compression Sets for Additive Rubbers

Vulcanizate (Designated by Additive)	Footnotes	(Blank Factor) F	Experimental Compression Set	Predicted Compression Set [a]	Difference Between Predicted and Experimental	Difference Required for Statistical Significance at 95% Level
9,10-Phenanthrenequinone	a	0.996	98	77	17	7
1,4-Naphthoquinone	a	0.997	99	77	20	7
N-(2-Aminoethyl)-N-ethyl-m-toluidine	a,b	0.976	66	77	9	12
1,3-Diphenyltriazine	a,b	0.974	67	77	11	12
N,N-Dimethyl-p-phenylenediamine	a,b	0.966	69	77	8	12
2,2'-Bipyridine	a,d	0.990	69	77	7	7
2-Amino-4-methylpyridine	a,b	0.976	70	77	6	7
8-Aminoquinoline	a,b	0.960	71	77	7	12
N,N-Diphenyl-p-phenylenediamine	a,b	0.98.	72	77	8	12
Triphenylstilbine	a,b	0.964	72	77	6	7
1-Naphthylamine	a,b	0.966	73	77	3	12
N-1-Naphthylethylenediamine	a,b	0.960	73	77	3	12
N,N-Dimethyl-p-1-naphthylaniline	a,b	0.995	73	77	6	12
2,4-Dinitrophenylhydrazine	a,b	0.971	73	77	6	7
N-Methyldiphenylamine	a,b	0.972	73	77	7	7
Tribenzylamine	a,b	0.976	73	77	7	12
Quinoline	a,b	0.974	73	88	6	12
2,2'-Biquinoline	a,b	0.97.	73	88	7	12
N,N,N',N'-Tetramethyl-p-phenylenediamine	a,b	0.997	74	77	7	12
o-Aminophenol	a	0.976	74	77	4	7
p-sec-Amylaniline	a,b	0.970	74	77	5	12
Di-iso-amylamine	a,b	0.995	74	77	5	12
Biphenyl	a	0.974	74	88	5	7
N-Methylaniline	a	0.995	74	88	7	12
Pyrene	a	0.976	74	88	6	7
1-Naphthylamine	a,b	0.995	74	77	6	12
Phenyl Sulfide	a	0.996	74	88	5	7
Fluoranthrene	a	0.970	77	88	6	7
N,N-Dimethyldodecylamine	a,b	0.994	77	77	3	12
Hydroquinone	a,b	0.978	77	77	3	7
Diphenylamine	a,b	0.970	77	77	4	7
3,5-Dimethylpyrazole	a,d	0.989	77	77	3	12
Acridine	a,b	0.972	77	77	5	12
2-Vinylpyridine	a,b	0.982	77	75	5	7
o-Phenylenediamine	a,b	0.974	77	85	8	12
1,2-Naphthoquinone	a	0.976	77	88	5	12
N,N-Di-n-propylaniline	a	0.993	77	77	3	7
Triphenyl Bismuthine	a	0.995	77	88	3	7
2,2-Diphenyl-1-picrylhydrazyl	a	0.974	77	88	4	12
2,4-Dinitro-6-phenyl-s-triazine	a	0.992	77	88	5	7
Butyl Disulfide	a	0.995	77	88	3	7
Phenanthrene	a,d	0.966	77	88	4	7

(continued)

TABLE 2 (Cont'd)

Compression Sets for Additive Rubbers

Vulcanizate (Designated by Additive)	Footnotes	(Black Factor)	Experimental Compression Set	Predicted Compression Set [e]	Difference Between Predicted and Experimental	Difference Required for Statistical Significance at 95% Level
1,3-Di-o-tolylguanidine	a,d	0.947	77	85	8	7
N-Phenyl-N'-isopropyl-p-phenylenediamine	a,b	0.994	77	81	4	7
N,N'-Diphenylbenzidine	a,b	0.974	77	80	3	12
Triphenylamine	a,b	0.976	77	79	2	12
p-Quaterphenyl	a,b	0.993	77	80	3	12
N-iso-Amylaniline	a,b	0.966	77	80	3	7
o-Terphenyl	a,b	0.997	77	81	3	12
N,N,N',N'-Tetramethylbenzidine	a,b	0.962	78	80	4	12
Carbazole	a,b	0.972	78	84	2	7
Phenyl Disulfide	a	0.992	78	80	6	7
p-Terphenyl	a,b	0.996	78	80	2	12
N,N'-Diphenylethylenediamine	a	0.974	78	79	2	7
Triphenylmethane	a	0.996	78	81	1	7
iso-Butyl Sulfide	a	0.991	78	79	3	7
p-Aminophenol	a,b	0.997	78	79	1	12
p-Phenylenediamine	a	0.976	78	77	-1	7
Chrysene	a	0.992	78	80	2	7
Diphenylmercury	a	0.985	78	74	-4	7
Cystine	a	0.997	78	78	0	7
Naphthalene	a	0.995	79	80	2	7
Phenol	a,b	0.991	79	77	-1	12
Hexamethylenetetramine	a,b	0.904	79	80	2	7
iso-Butyl Disulfide	a,d	0.995	79	80	-1	12
2-Benzylpyridine	a	0.966	79	82	3	7
Dicyclohexylamine	a,d	0.990	79	78	-1	7
4,4'-Oxydiphenol	a	0.995	79	82	3	7
Dibutyltin Dichloride	a,c,b	0.986	79	80	-1	12
N,N-Dimethylaniline	a,b	0.972	79	80	1	7
o-Terphenyl	a,b	0.995	79	80	1	12
2-n-Amylpyridine	a	0.974	80	80	0	12
Tri-iso-amylamine	a,b	0.995	80	79	0	12
Anthraquinone	a	0.994	80	79	-1	7
Resorcinol	a	0.904	80	79	-1	7
Aniline	a	0.995	80	82	2	12
Butyl Sulfide	a,c	0.995	80	79	-1	7
p,p'-Biphenol	a	0.994	81	82	2	7
Carbothene Knekt 23	a,b	0.993	81	79	-1	12
Tetrabutyl Tin	a,b	0.993	81	82	3	7
N,N'-Dicarbethoxyhydrazine	a	0.996	81	81	0	7
Tetraphenyl Tin	a,b	0.995	81	79	-2	12
Indocarbon CL	c,b	0.996	81	80	-1	7
Anthracene	a	0.995	82	80	-2	12
N,N'-Dimethyl-p-phenylenediamine	a,b	0.980	82	79	-3	12
Benzidine	a,b	0.9??	82	79	-3	12

(Continued)

TABLE 2 (Cont.)

Compression Sets for Additive Rubbers

Vulcanizate (Designated by Additive)	Footnotes	(Black Factor) F	Experimental Compression Set	Predicted Compression Set [e]	Difference Between Predicted and Experimental	Difference Required for Statistical Significance at 95% Level
Tetraethyl Orthotitanate	a	0.971	82	85	3	7
Dibutyltin Diacetate	a	0.981	82	80	-2	7
Hydrazine Sulfate	a	0.987	83	79	-4	7
Triphenyltin Chloride	a	0.981	84	80	-4	7
Tetramethyl Orthosilicate	a	0.988	85	81	-4	7
1,2,3-Triisobutriazine	a	0.973	85	84	-1	7
Copper Phthalocyanine	c,b	0.990	85	83	-2	12
2-Aminobenzimidazole	a,d	0.982	86	91	5	7
Phthalocyanine	c,b	0.982	87	84	-3	12
a-Anthraphenol	a,b	0.992	88	85	-3	7
Didodecyl Selenide	b	0.974	88	83	-5	12
Palmroglucinol	a,f	0.982	90	84	-4	7
Graphite	a	0.990	90	83	-7	12
1,4-Benzoquinone	a	0.967	96	91	-5	7

a. The chemical formula is given in Eastman Organic Chemicals List No. 42, Distillation Products Industries, Rochester 3, N. Y.

b. Compression set was calculated from previously obtained data[1] and the formula of the present report. Specimens were irradiated with gamma radiation from spent fuel elements of the General Electric Test Reactor at Vallecitos, California.

c. The chemical formula is given in reference 3.

d. Compression set data obtained previously[1] for vulcanizates containing this additive were not used. Instead, new test specimens were prepared. The compression set value given is the average of a quintuplicate experiment.

e. Equation 3 was used to calculate the predicted compression set.

The blank factor, F, is defined by Eq. 3

$$F = \frac{1}{n} \sum_{1}^{n'} \frac{\ell_{sc}}{\ell_{oc}} \tag{3}$$

where ℓ_{sc} = Set length for a non-irradiated control specimen.
ℓ_{oc} = Original length for a non-irradiated control specimen.
n = Number of control specimens.

When the blank factor, F, approaches unity, Eq. 2 becomes the simplified one used in the previous study.[1] The vulcanizates evaluated for compression set in the previous study have been re-evaluated herein. Their compression sets have been recalculated by using the data of the previous study in conjunction with Eq. 3.

RESULTS AND CONCLUSIONS

Perhaps the most significant contributions of this and the previous study are the quantitative relationships between radiation-induced compression set and cure. The fact that both state of cure and presence of rubber additives affect compression set makes anti-rad evaluation more complex than was previously supposed and subject to a wider degree of experimental error.

Cure Study

The relationship between compression set induced by a 10^8 r dose and degree of initial crosslinking (vulcanization) has been determined by two procedures. In Procedure I, rubber stocks were used having different degrees of crosslinking brought about by different cure times. In Procedure II, stocks were used having different degrees of crosslinking brought about by incorporating an additive.

Figure 1 shows the relationship resulting from Procedure I. The curve is the regression line of the compression set and crosslinking data of Table 1 and is defined by Eq. 4:

$$S = -0.66 \times 10^{-18} \, C_o + 95.1 \tag{4}$$
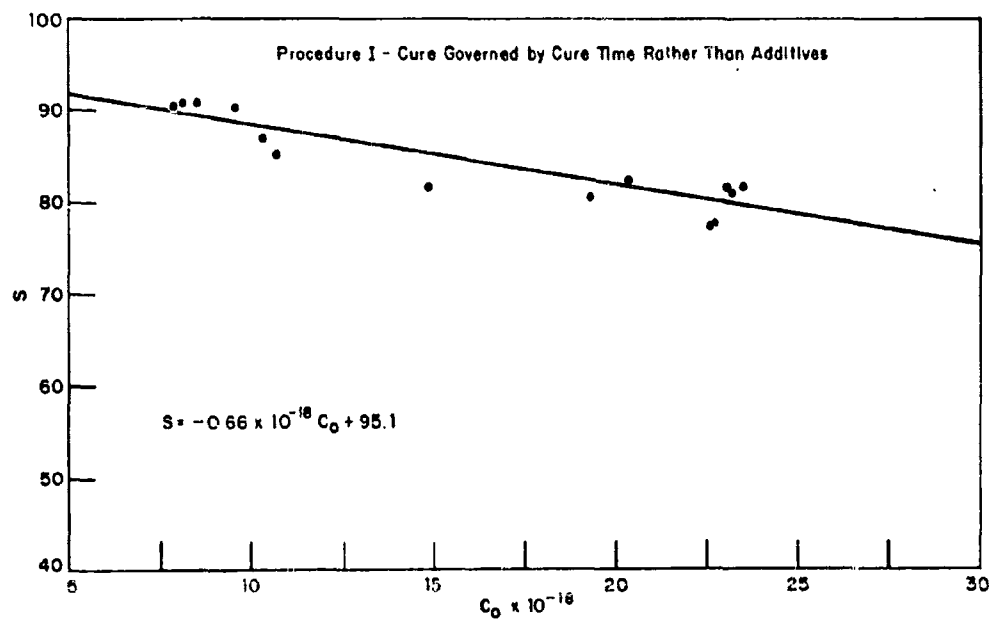
Fig. 1 Compression Set at 10^8 r Versus Pre-Irradiation Crosslinks - Procedure I.

where S = Percent compression set.

      C_0 = Number of pre-irradiation crosslinks per gram of cylindrical specimen.

Each data point represents the average from quintuplicate compression sets and quintuplicate solvent-swollen specimens. The blank factor, F (Eq. 3), was determined with triplicates. The standard error in estimating S from C_0 by Eq. 5 is 2.1.[5]

Figure 2 shows the relationship resulting from Procedure II. The curve is the regression line of the experimental compression set and crosslinking data of Tables 2 and 3 (0 dose) for those rubbers prepared specifically for this second compression set study, those not identified by footnote symbol b in Table 2. The curve is defined by Eq. 5:

$$S = -0.77 \times 10^{-18} C_0 + 95.2 \tag{5}$$

Each data point represents the average from triplicate compression sets and triplicate solvent-swollen specimens. The blank factor (Eq. 3) was determined with triplicates.

The relationships between compression set and initial cure defined by Eq. 4 (Procedure I) and Eq. 5 (Procedure II) have identical intercepts and vary by 14 % in slope. This is a reflection of the fact that the majority of the chemical additives in Procedure II exhibited little or no anti-rad or radiation-sensitizing characteristics. Procedure I, involving no chemical additives, is considered to be the more basic procedure; accordingly, Eq. 4 is used herein for predicting compression set values from corsslinking values.

The relationship between compression set and initial cure was also determined through Procedure II by combining data of the previous and present study, that is, by using compression set and crosslinking data for all additive rubbers listed in Table 2. The data of the previous study were made to conform to those of the present one by re-calculating compression sets for unheated specimens. Equation 6 is the regression line.

$$S = -0.88 \times 10^{-18} C_0 + 97.5 \tag{6}$$

Equation 6 is not considered as reliable as Eqs. 4 and 5, since the crosslinking values of the previous study were determined with only a single specimen.
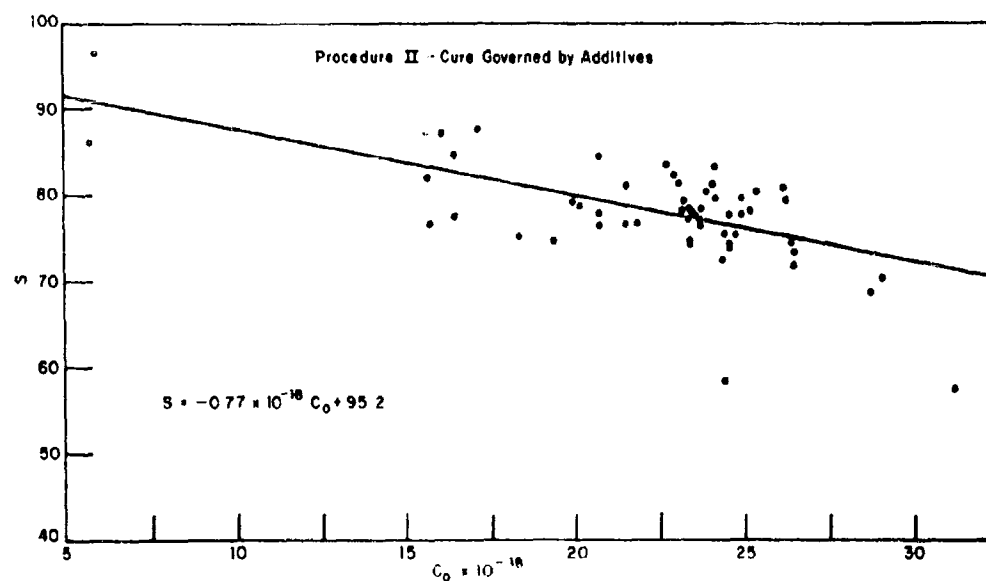
Fig. 2 Compression Set at 10^8 r Versus Pre-Irradiation Crosslinks -
Procedure II

Anti-Rad Study

Anti-rad behavior is demonstrated when the experimental compression set is significantly less than that predicted from the initial cross-linking by Eq. 4 (Fig. 1). A comparison of experimental and calculated compression sets in Table 2 shows with 95 % confidence that phenanthrene-equinone and 1,4-naphthoquinone definitely qualify as anti-rads at a 10^8 r dose, but that the following additives barely qualify at this level of confidence and are, thus, of questionable status: 2, 2'-bipyridine; acridine; 1,2-naphthoquinone; 1,3-di-o-tolylguanidine.

It is of interest that 9,10-phenanthrenequinone and 1,4-naphthoquin-one exhibit anti-rad behavior, decreasing compression set in rubber at 10^8 r; that 1,2-naphthoquinone barely or questionably does; and that 1, 4-benzoquinone and anthraquinone do not.

2,2-Diphenyl-1-picrylhydrazyl was not an anti-rad. This material exists completely as diphenylpicrylhydrazyl radicals in the solid state. One would expect these radicals in a vulcanizate to react with free radicals produced in the rubber hydrocarbon by irradiation and, thus, block radical-engendered crosslinking and scission. Probably diphenyl-picrylhydrazyl radicals were never present in the vulcanizate, having been destroyed by reacting with radicals produced in the rubber by mill-mixing and curing.

No anti-rads have ever been found which will perform at a 10^9 r dose. Because 10^9 r would require a 5300-hr exposure to the cobalt-60 source, the potential anti-rads were screened at 10^8 r with the intention of testing at 10^9 r those which showed promise. 9,10-phenanthrenequin-one and 1,4-naphthoquinone qualify for testing at 10^9 r. Only anti-rads which cause an appreciable reduction in compression set at 10^9 r would be of practical value.

Chain Scission and Crosslinking

The total number of crosslinks per gram for a compressed specimen before irradiation and after doses of 10^7 and 10^8 r are given in Table 3. These data show that, depending upon the additive, crosslinking may pre-dominate over or be balanced by chain scission up to 10^7 r, but that crosslinking always predominates at 10^8 r. Crosslinking increases enor-mously between 10^8 and 10^9 r, so that specimens become brittle or glassy, or shrink to give compression sets over 100 %.

Table 3 gives radiation yields for scission of the original network and radiation yields for concurrent crosslinking to form a new network conforming to the compressed state. These yields, G(S) and G(C),

TABLE 3

Crosslinking Values and Radiation Yields

Vulcanizate (Additive Rubbers Designated by Additive)	Foot-notes	Total Crosslinks Per Gram C_0 (x 10^{-18}) 0 Dose	C (x 10^{-18}) 10^7 r	10^8 r	Decrease in Vulcanization Crosslinking per Gram, ΔC_0 for 10^8 r Dose (x 10^{-18})	Radiation-Induced Crosslinks Per Gram, C_r for 10^8 r Dose (x 10^{-18})	Radiation Yield Between 0 to 10^7 r G(Scission)	G(Crosslinking)
9,10-Phenanthrenequinone	a	31.2	29.3	34.7	16.6	20.3	1.2	0.81
1,4-Naphthoquinone	a	24.4	23.9	28.8	13.0	17.1	0.55	0.41
2,2'-Bipyridine	b,c	28.7	30.7	38.1	17.7	26.9	1.0	1.3
2-Amino-4-methylpyridine	b,c	29.0	30.5	39.1	18.6	28.0	0.98	1.1
Triphenylstilbine	a	26.4	26.4	38.0	16.7	28.1	1.6	1.5
2,4-Dinitrophenylhydrazine	a	26.3	27.8	34.8	15.5	25.6	0.27	0.81
o-Aminophenol	a	26.4	28.4	35.6	17.1	26.3	0.68	0.98
Biphenyl	a	24.5	28.0	35.3	15.7	26.4	0.34	0.94
Pyrene	a	23.3	27.0	33.6	14.8	25.2	0.62	1.2
Phenyl Sulfide	a	24.5	27.3	32.6	16.5	24.5	0.69	1.1
Fluoranthene	a	23.3	26.2	30.9	15.4	23.2	0.65	1.1
Hydroquinone	a	26.3	30.4	36.9	17.0	27.7	0.39	1.1
Acridine	b,c	19.3	23.8	33.4	11.4	25.4	0.56	1.3
1,2-Naphthoquinone	a	18.3	21.5	34.1	10.7	26.6	0.45	0.97
Triphenyl Hexathane	a	24.7	24.6	36.3	16.5	27.8	1.3	1.3
2,2-Diphenyl-1-picrylhydrazyl	a	24.4	26.3	32.3	17.3	24.7	0.63	0.85
Butyl Disulfide	a	20.7	22.0	24.6	15.3	19.1	0.93	1.1
Phenanthrene	a	23.7	27.0	32.4	16.2	25.0	0.72	1.3
N-Cyclohexyl-N'-phenyl-p-phenylenediamine	b,c	21.5	24.0	31.8	14.8	25.0	0.46	0.89
1,3-Di-o-tolylguanidine	b,c	15.7	19.0	25.4	11.3	20.8	0.71	1.2
N-Phenyl-N'-isopropyl-p-phenylenediamine	c	21.8	24.1	33.2	14.6	25.8	0.47	0.83
p-Quaterphenyl	a	23.6	27.4	38.1	15.0	29.7	0.79	1.4
m-Terphenyl	a	23.3	26.5	34.7	15.8	27.0	0.76	1.3
Phenyl Disulfide	a	16.4	17.8	21.8	11.8	17.1	0.98	0.83

(Continued)

195

TABLE 3 (Cont.)

Crosslinking Values and Radiation Yields

Vulcanizate (Additive Rubber Designated by Additive)	Foot-notes	Total Crosslinks Per Gram c_0 ($\times 10^{-18}$)		c ($\times 10^{-18}$)	Decrease in Vulcanization Crosslinks per Gram, Δc_0 for 10^8 r Dose ($\times 10^{-18}$)	Radiation-Induced Crosslinks Per Gram, c_r for 10^8 r Dose ($\times 10^{-18}$)	Radiation Yield between 0 to 10^7 r	
		0 Dose	10^7 r	10^8 r			G(scission)	G(crosslinking)
p-Terphenyl	a	23.5	27.1	36.5	15.6	28.5	0.86	1.5
Triphenylmethane	a	24.5	27.7	35.3	16.9	27.7	0.73	1.3
iso-Butyl Sulfide	a	20.7	23.0	26.9	14.9	21.2	0.81	1.2
p-Aminophenol	a	24.9	27.8	38.0	17.2	29.8	0.76	1.2
Chrysene	a	23.4	27.5	35.8	15.8	28.3	0.80	1.5
Diphenylmercury	a	31.7	34.3	35.7	24.6	28.5	1.2	1.7
Cystine	a	25.2	27.4	37.7	17.4	29.6	0.74	1.2
Naphthalene	a	23.1	25.4	35.8	15.7	28.2	0.66	1.2
Phenol	a	23.3	26.0	39.1	15.7	31.2	1.1	1.5
iso-Butyl Disulfide	b,c	23.7	27.1	35.8	16.5	28.1	0.79	1.3
Dicyclohexylamine	b,c	20.1	27.9	33.9	14.4	28.2	0.56	1.9
4,4'-Oxydiphenol	a	26.2	30.4	38.6	18.9	30.9	0.83	1.4
Dibutyltin Dichloride	a	19.9	24.0	28.9	14.5	23.3	0.85	1.5
o-Terphenyl	a	23.2	25.5	34.2	16.4	27.3	0.55	1.2
Anthraquinone	a	24.1	26.6	34.3	17.7	27.5	0.83	1.2
Resorcinol	a	24.9	27.7	37.7	17.7	30.4	0.95	1.4
Butyl Sulfide	a	23.8	27.1	36.2	16.8	29.3	0.86	1.4
p,p'-Biphenol	a	25.3	29.1	35.4	19.0	28.7	0.96	1.5
Tetrabutyl Tin	a	26.1	29.0	36.3	20.4	29.6	0.81	1.2
N,N'-Dicarbethoxydiamine	a	21.5	24.5	38.0	14.9	31.1	1.2	1.6
Tetraphenyl Tin	a	24.0	27.6	36.0	17.7	29.6	0.92	1.4
Anthracene	a	23.0	26.4	36.8	16.5	30.2	0.91	1.4
Tetramethyl Orthotitanate	a	15.6	18.1	36.1	10.3	30.5	0.98	1.3
Dibutyltin Diacetate	a	22.9	26.8	26.0	18.6	21.8	0.55	1.2
Hydrazine Sulfate	a	24.1	25.4	36.6	18.4	30.9	1.1	1.3
Triphenyltin Chloride	a	22.7	25.6	36.8	17.4	31.2	1.2	1.6
Tetramethyl Orthosilicate	a	20.7	23.7	35.7	15.2	30.6	0.95	1.5
1,2,3-Trimethoxybenzene	a	16.4	20.7	28.2	12.7	24.5	0.70	1.4

(Continued)

TABLE 3 (Cont'd)

Crosslinking Values and Radiation Yields

Vulcanizate (Additive Rubbers Designated by Additive)	Foot-notes	Total Crosslinks Per Gram C_0 (x 10^-18) C (x 10^-18)			Decrease in Vulcanization Crosslinking per Gram, ΔC_0 for 10^8 r Dose (x 10^-18)	Radiation-Induced Crosslinking Per Gram, C_r for 10^8 r Dose (x 10^-18)	Radiation Yield Between 0 to 10^7 r	
		0 Dose	10^7 r	10^8 r			G(Scission)	G(Crosslinking)
2-Aminobenzimidazole	b,c,d	5.7	12.3	23.4	-	-	-	-
n-Aminophenol	a	16.0	20.8	32.4	15.6	32.0	0.79	1.6
Phloroglucinol	a	17.1	23.1	32.7	15.2	31.0	0.62	1.7
1,4-Benzoquinone	a	5.8	12.6	24.7	5.7	24.6	0.23	1.4
Stock 1 (6.5 min. cure-no additive)	c,d	7.8	22.0	27.7	-	-	-	-
Stock 2 (7 min. cure-no additive)	c,d	8.1	20.6	27.4	-	-	-	-
Stock 3 (7.5 min. cure-no additive)	c,d	8.5	23.8	26.2	-	-	-	-
Stock 4 (8 min. cure-no additive)	c,d	9.5	23.1	28.9	-	-	-	-
Stock 5 (8.5 min. cure-no additive)	c,d	10.3	23.3	27.6	-	-	-	-
Stock 6 (9 min. cure-no additive)	c,d	10.7	24.4	28.5	-	-	-	-
Stock 7 (9.5 min. cure-no additive)	c,d	14.8	25.1	28.4	-	-	-	-
Stock 8 (10 min. cure-no additive)	c,d	20.3	28.1	31.0	-	-	-	-
Stock 9 (15 min. cure-no additive)	c	23.0	29.3	32.9	17.2	27.2	0.18	1.3
Stock 10 (20 min. cure-no additive)	c	23.5	28.6	33.8	17.7	27.5	0.60	1.4
Stock 12 (25 min. cure-no additive)	c	23.2	29.0	35.8	16.4	29.2	0.53	1.5
Stock 13 (30 min. cure-no additive)	c	22.7	28.2	35.0	14.4	27.6	0.34	1.3
Stock 14 (35 min. cure-no additive)	c	22.6	28.4	35.8	15.0	28.0	0.38	1.4

a. Each value of C_0 x 10^-18 and C x 10^-18 is the average of a triplicate solvent swelling experiment. Values of ΔC_0 x 10^-18, C_r x 10^-18 and radiation yields were calculated by combining data from triplicate solvent swelling and triplicate compression set experiments.

b. The results for this additive rubber were not taken or re-calculated from the previous report.[1] New test specimens were prepared for this study.

c. Each value of C_0 x 10^-18 and C x 10^-18 is the average of a quintuplicate solvent swelling experiment. Values of ΔC_0 x 10^-18, C_r x 10^-18 and radiation yields were calculated by combining data from quintuplicate solvent swelling and quintuplicate compression set experiments.

d. C_r values could not be calculated. Significant specimen flow under compression made the equations for calculating ΔC_0, C_r and G values inapplicable. Values of G(Scission) turned out negative.

respectively, are defined as the number of chains scissioned or net crosslinks formed per 100 ev of absorbed energy. $G(S)$ and $G(C)$ do not vary significantly with additive. They accord well with the yields of the previous report,[1] and the average values of Table 3 are 0.75 and 1.3, respectively. Radiation yields were determined by the method combining compression-set and solvent-swelling measurements[1] for 10^7 r. They are not determined with a dose as great as 10^8 r because their non-linearity with dose leads to an unrealistic average value. They are not determined with a dose less than 10^7 r because specimen set would be too small for reliable measurement. Furthermore, they are not determined reliably when there is appreciable specimen flow under compression, since the equation (Eq. 11, ref. 1) that incorporates the set length ℓ_s and is required for calculating radiation yields is theoretically inapplicable when specimens flow. Specimen flow is revealed by blank factors which depart significantly from unity. This inapplicability is actually seen when values of $G(S)$ turn out to be negative in cases where specimens flow. The blank factors of Table 1 show that specimen flow is significant below a pre-irradiation cross-linking density of 20×10^{18} crosslinks per gram.

Both the number of pre-irradiation (vulcanization) crosslinks scissioned by radiation and the number of crosslinks formed by radiation in the compressed state depend upon the degree of initial cure. The relationships are defined by Eqs. 7 and 8, and are depicted in Fig. 3:

$$\Delta C_o = 0.60 \; C_o + 2.4 \times 10^{18} \tag{7}$$

$$C_r = 0.26 \; C_o + 21.5 \times 10^{18} \tag{8}$$

where C_o = Number of initial (vulcanization) crosslinks per gram of specimens.

   ΔC_o = Number of vulcanization crosslinks scissioned per gram of specimen by 10^8 r.

   C_r = Number of crosslinks engendered per gram of specimen in the compressed state by 10^8 r.

These curves are the regression lines of the data for ΔC_o, C_r, and C_o in Table 3, except that the data for 9, 10-phenanthrenequinone, 1,4-naphthoquinone, and 1,4-benzoquinone were omitted since the former two were anti-rads and the latter had a low cure conducive to specimen flow. These relationships result from the fact that as initial crosslinking density increases, the probability of scission increases and the probability for crosslinking increases due to greater proximity of hydrocarbon chains.

198
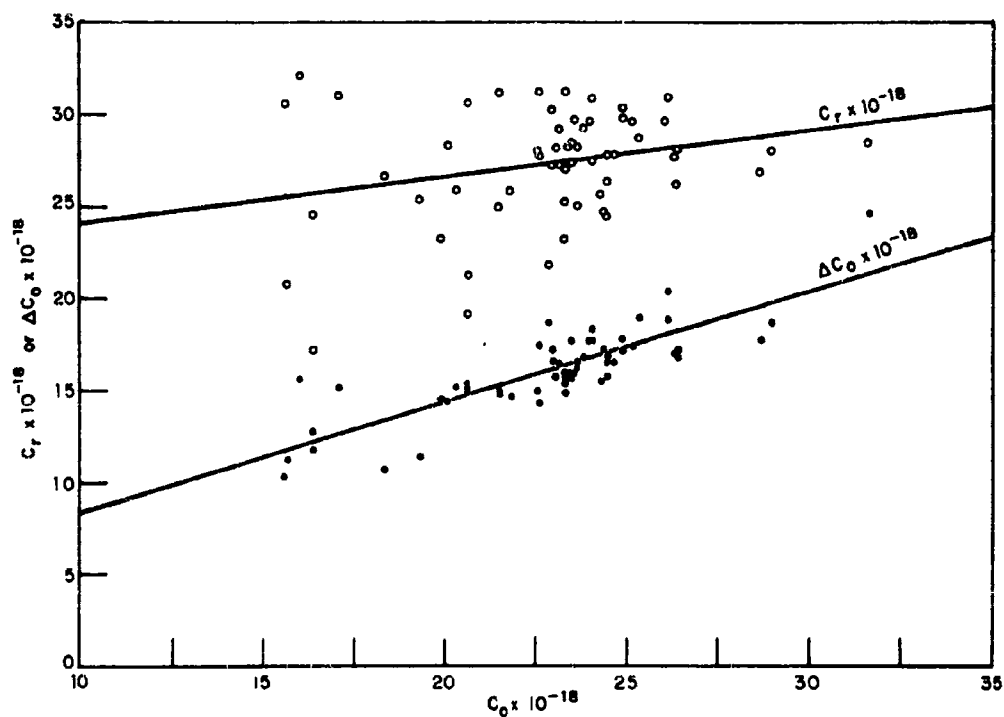
Fig. 3 Crosslinks Formed in Compressed State (C_r) by 10^8 r Versus Pre-
Irradiation Crosslinks
and
Vulcanization Crosslinks Scissioned (ΔC_o) by 10^8 r Versus Pre-
Irradiation Crosslinks

Anti-rads may be identified by incorporating them into pellets and measuring the sum of ΔC_0 and C_r. There is evidence of anti-rad behavior when the experimental sum is significantly less than that predicted from Eqs. 7 and 8 on the basis of degree of cure. The basis for this is that cleavage of the initial (vulcanization) network and crosslinking to form a new network of the compressed state both promote set. An anti-rad must function by minimizing these processes which are measured by ΔC_0 and C_r. 9,10-Phcnanthrenequinone and 1,4-naphthoquinone were identified as anti-rads by means of compression set. Their values of $(\Delta C_0 + C_r)$ are 36.9×10^{18} and 30.1×10^{18}, respectively (Table 3), which are below the values predicted from degree of cure (50.6×10^{18} and 44.7×10^{18}, respectively) and which differ from the predicted values at the 95 % confidence level.

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ELASTOMERS RESISTANT TO ULTRAVIOLET VACUUM AND HIGH TEMPERATURE

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The rapid development of our space capabilities has created an unprecedented demand for materials of construction which are stable under rather the exotic conditions of temperature, pressure, and ultraviolet radiation which can reasonably be anticipated in the aerospace environment. It has been our privilege at the Armour Research Foundation to participate in this program, directing our particular attention to the behavior of elastomers. Since we found few methods for characterizing the decomposition reaction, we were obliged to devise methods particularly suited to the quantitative, or at least semiquantitative, description of the reactions which were observed.

Only a few years ago, it was commonly believed that organic polymers would "sublime" in vacuum, and the effect of moderate temperatures and short-wavelength (i. e. , > 2000 A) ultraviolet radiation were similarly overestimated. In our opinion, the most significant factor in the aerospace environment is the absence of oxygen; even small amounts of oxygen materially change both the rate and the nature of the degradative process. Accordingly, the attention which must be devoted to valid experimental procedures in a study of this nature is perhaps the single most important, difficult, and time-consuming aspect of the problem. With this thought in mind, we shall describe some of the work which we have done on the degradation of elastomers in a simulated space environment.

The irradiation chamber (Fig. 1) consists of a mild-steel cylinder 24 in. high and 24 in. in diameter. AH-6 lamps (Fig. 2), quartz-jacketed and cooled with demineralized water, are mounted in the head. Heat is supplied by a 500-w General Electric quartz incandescent lamp. Samples are mounted in tension, radially, on a turntable (Fig. 3) beneath the lamps. Samples are rotated to make all positions equivalent and to give greater flexibility in adding
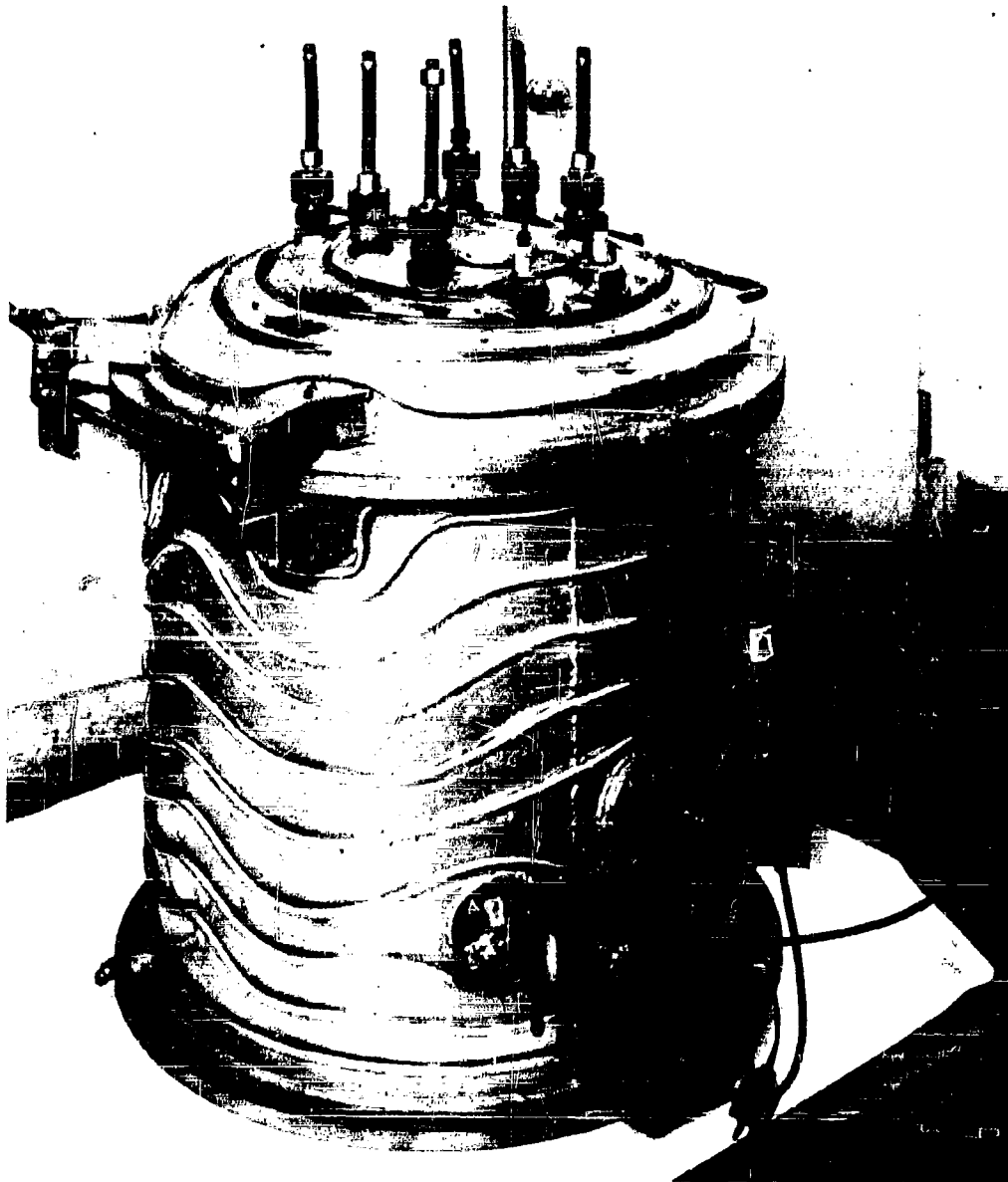
Fig. 1. Irradiation Chamber
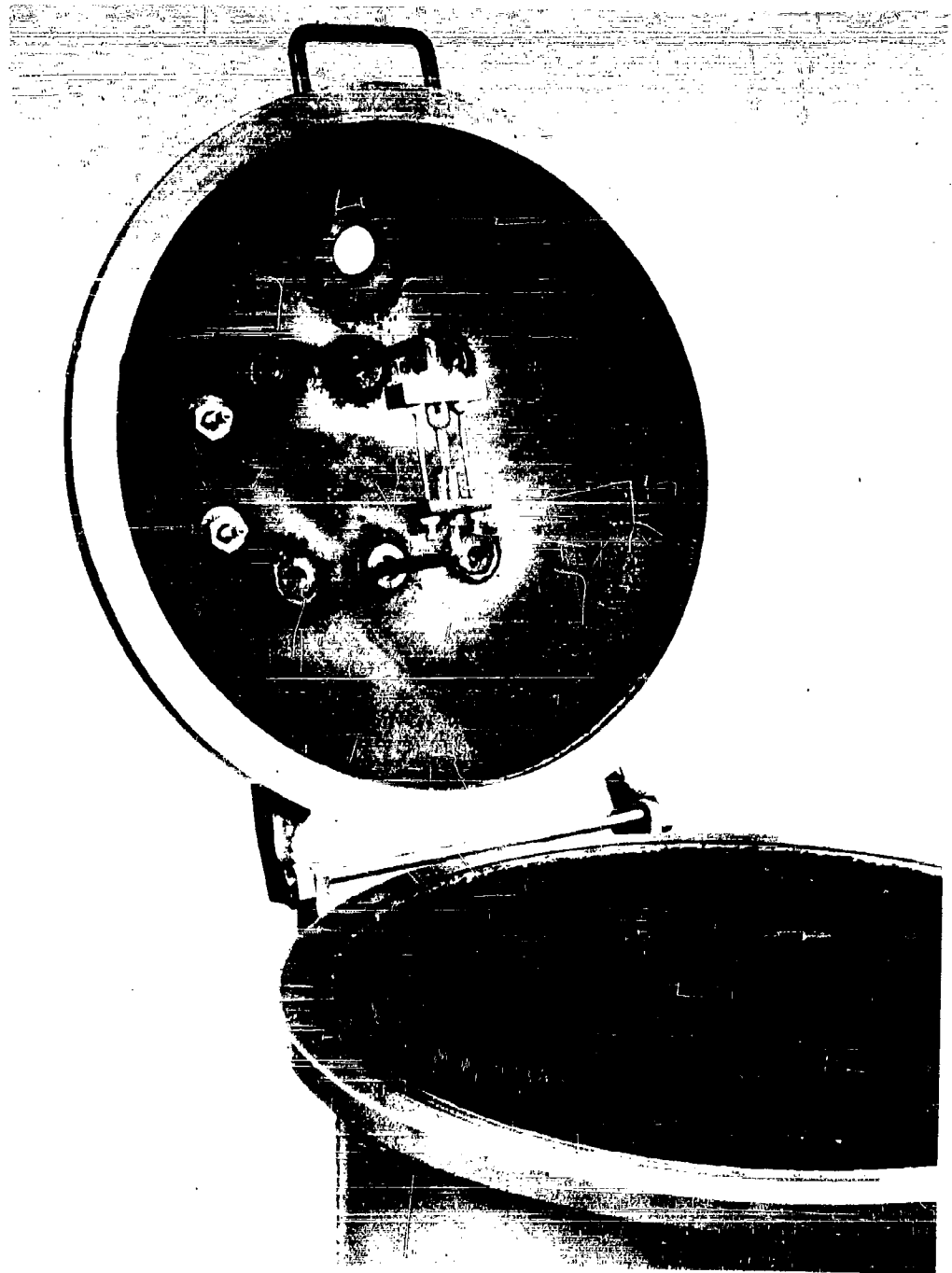
Fig. 2.   Inside of Head of Irradiation Chamber
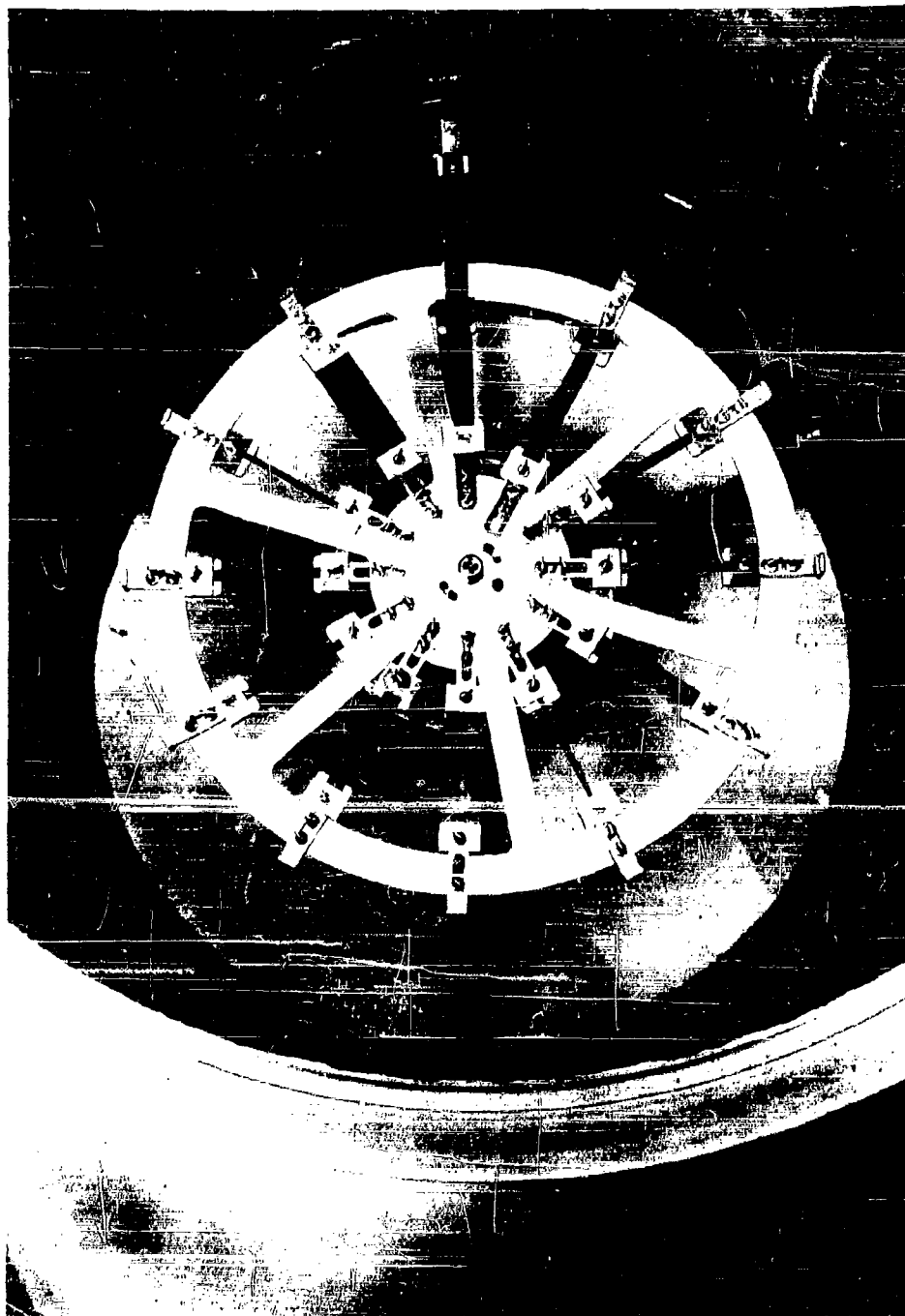
Fig. 3. Samples Mounted on Turntable
in Irradiation Chamber

ultraviolet lamps or incandescent heating lamps. Rotation is effected through a 12-point Geneva drive. As each sample reaches the measuring station in turn, the force required to maintain constant elongation is measured and the surface temperature is read by a thermocouple mounted on a cam-actuated spring-steel lever.

Absolute values of the light intensities are obtained in the chamber from a temperature-compensated wide-angle thermopile before and after each run. The constancy of radiation during the run is monitored by an externally mounted thermopile which senses a constant fraction of the radiation through a quartz port in the head.

Since a single force transducer was used to measure all the samples, variations in elastic modulus were compensated for by varying the width of the samples, as seen in Fig. 3. Samples were elongated 25%; the initial force was approximately 200 g. Stress decay was chosen as the parameter for measuring degradation because it was adaptable to continuous measurement in situ. Since this is a bulk property and since we could predict that degradation would attenuate through the sample with the light intensity, thin samples were chosen to maximize the surface-to-bulk ratio. However, the thinnest samples which could be obtained from commercial rubber molders were 0.010 in., and they were heavily pigmented. The reaction was predictably confined to the upper surface, and stress-decay measurements proved insensitive (Fig. 4). However, when the irradiated samples were released from tension, many showed distinct curling after comparatively short periods of exposure. This was evidently caused by a permanent set in the irradiated surface.

Andrews et al. (1) have developed equations relating permanent set to the decay of old cross-links and to the formation of a new network at equilibrium in the extended position:

$$\% \text{ permanent set} = \frac{L_s - L_u}{L_x - L_u}\ 100$$

where L_x is the extended length, L_u is the original length, and L_s is the final length, after set.

In terms of chemical bonds, permanent set can be expressed as

$$\% \text{ permanent set} = \left[\left(\frac{C_1}{(S_u/S_x)\ C_2 + 1}\right)^{1/3} - 1\right] C_3$$
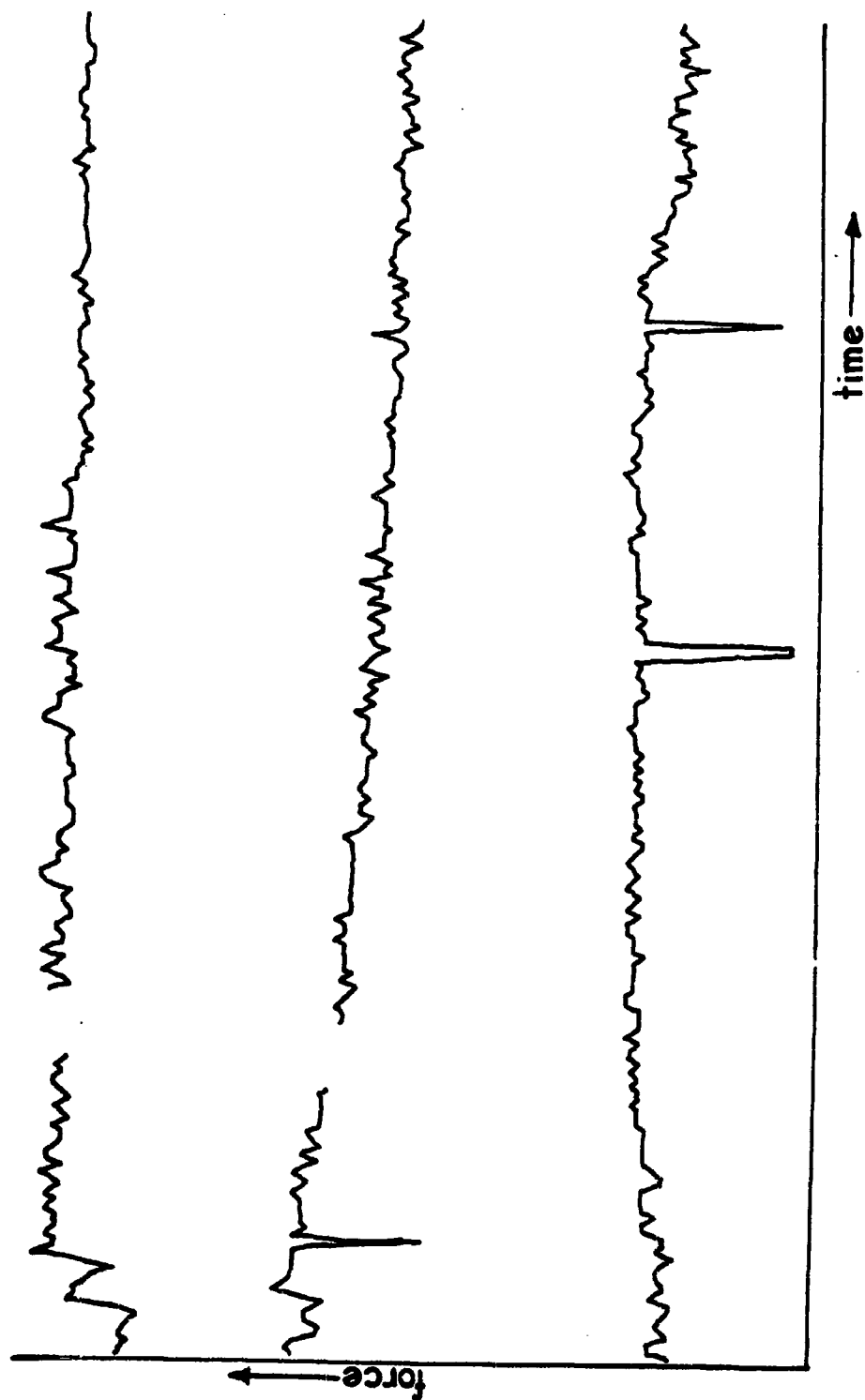
STRESS - TIME CURVES

Fig. 4. Stress-Time Curves

where S_u is the number of chains per cubic centimeter at equilibrium in the unextended length, S_x is the number of network chains per cubic centimeter at equilibrium in the extended length, and

$$C_1 = \left(\frac{L_x}{L_u}\right)^3 - 1 \qquad C_2 = \left(\frac{L_x}{L_u}\right)^2 \qquad C_3 = \frac{100}{(L_x/L_u) - 1}$$

The conversion of observed curvature to permanent set in the top surface was approximated by considering the exposed sample as a two-ply model, one ply being the exposed, degraded layer and the other the unaltered bulk of the material, as shown in Fig. 5.

Let t_1, E_1, and I_1 be the thickness, modulus of elasticity, and moment of inertia of the top layer, and t_2, E_2, and I_2 be the same quantities for the bottom layer. Let e_o denote the difference in unit length between the two layers if they were separated, and let b denote the width of the sheet. Axial forces T and bending moments M_1 and M_2 would be required to bring the separated plies to match. Assume a common $1/\rho$, ρ being the radius of curvature. Then:

$$\frac{M_1}{E_1 I_1} = \frac{M_2}{E_2 I_2} = \frac{1}{\rho} \tag{1}$$

where

$$I_1 = \frac{b t_1^3}{12}$$

and

$$I_2 = \frac{b t_2^3}{12}$$

$$M_1 + M_2 = \frac{T}{2} (t_1 + t_2) \tag{2}$$

$$\frac{T}{E_1 b t_1} + \frac{t_1}{2\rho} + \frac{T}{E_2 b t_2} + \frac{t_2}{2\rho} = e_o \tag{3}$$

Rearrangement of Eq. 1 yields:
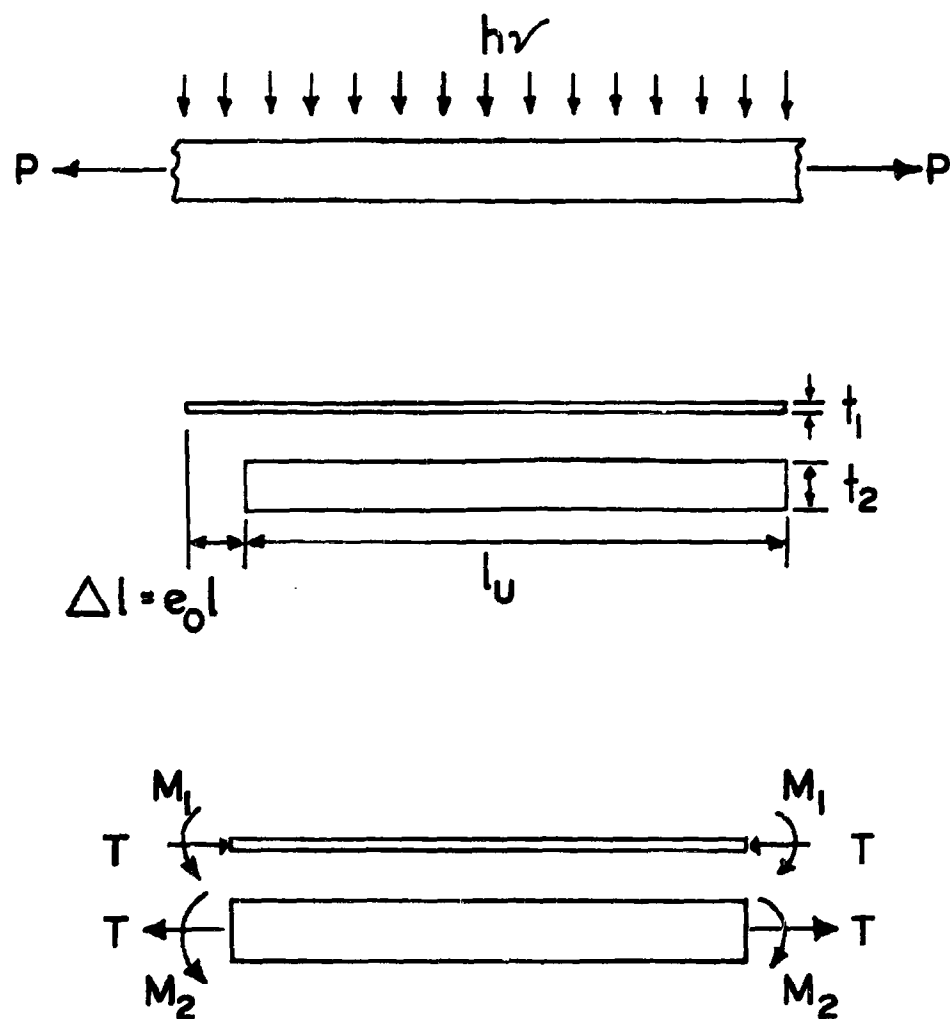
Fig. 5. Analysis of Permanent Set of Surface

$$\frac{M_1 + M_2}{E_1 I_1 + E_2 I_2} = \frac{1}{\rho}$$

Substituting in Eq. 2 yields:

$$\frac{T}{2} \cdot \frac{t_1 + t_2}{E_1 I_1 + E_2 I_2} = \frac{1}{\rho}$$

Thus:

$$T = \frac{2}{\rho} \frac{E_1 I_1 + E_2 I_2}{t_1 + t_2}$$

This relationship can be substituted in Eq. 3 to yield:

$$e_o = \left[\frac{2}{\rho} \frac{E_1 I_1 + E_2 I_2}{(t_1 + t_2) b} \left(\frac{1}{E_1 t_1} + \frac{1}{E_2 t_2} \right) \right] + \frac{t_1 + t_2}{2 \rho}$$

Since $e_o L_u = \Delta L = L_s - L_u$, the experimental quantity necessary for permanent set measurements, we now have the necessary data for such measurements if t_1, t_2, E_1, and E_2 can be determined.

The justification for this simple model, when experience indicates that the extent of degradation decreases more or less logarithmically without a finite boundary, is that a determination of the extent of degradation as a function of depth in the film is a research project in its own right. We have therefore chosen to use an effective thickness of the degraded layer and approximate its average mechanical properties.

Determination of this average thickness, t_1 in the equations above, is obviously difficult. Our solution has been to stretch the samples with their brittle, inextensible top layers to an $(L_x - L_u)/L_u$ of approximately 0.5. The top surfaces develop cracks, whose depths can be measured by making plastic replicas. The depth of these cracks is taken as t_1, and t_2 is the difference between the initial t and t_1.

We now have a value of S_u/S_x after exposure. We can determine that $S_{u_o} - S_u$ must be very small from the lack of appreciable stress relaxation, although this requires that the factor t/t_1 be used to convert the stress relaxation, which is occurring only in the surface, to $(S_{u_o} - S_u)/S_{u_o}$ for the degraded layer itself. Since t_1 is at best an approximation, this value is only slightly better than an order-of-magnitude estimate. By way of corroboration, there is no weight loss in these samples; appreciable chain scission should

209

result statistically in the formation of some volatile fragments.

The quantity $(S_u + S_x)/S_{uo}$ is a measure of the cross-link density in the irradiated surface. In more readily visualized quantities, this is a determination of the predominance of the scission or the cross-linking reaction. This quantity was investigated by gravimetric swelling measures; an irradiated sample was compared with one that had not been exposed. The elastomers were weighed, immersed in a high-boiling swelling solvent, and reweighed.

Again assume a two-ply model, with t, t_1, and t_2 having the original meanings. W_{eo} is the weight of unswollen, exposed film; W_{es} is the weight of swollen, exposed film; W_{uo} is the weight of unswollen, unexposed film; and W_{us} is the weight of swollen, unexposed film. Then $W_{us} - W_{uo}$ is the weight imbibed by unexposed film (X_u), and $W_{es} - W_{eo}$ is the weight imbibed by exposed film (X_e). $X_u (W_{eo}/W_{uo}) = X_{uc}$ is the weight imbibed, corrected to the same initial weight as the exposed film. Of X_{uc} grams imbibed, $X_{uc} (t - t_1)/t$ is imbibed by the lower layer, and this quantity is the same for both films. The weight absorbed by the top layer of the exposed film is thus $X_e - X_{uc} [(t - t_1)/t]$ The weight absorbed by the top layer of the unexposed film is $X_{uc} (t_1/t)$. Therefore the ratio of cross-link density in the exposed and unexposed layers is:

$$X_{u_c}\left(\frac{t_1}{t}\right)\bigg/X_e - X_{u_c}\left(\frac{t - t_1}{t}\right)$$

Values calculated from these determinations range from 1.25 to 8, depending on the elastomer and the exposure conditions.

An alternative method is based on the observation that most of the exposed films curl when placed in a swelling solvent. This is a rapid qualitative test for the predominance of cross-linking over scission. However, it can be made reasonably quantitative by application of calculations similar to those for the permanent set determinations and substitution of the proper physical constants for swollen film. There is one additional complication. Swelling is assumed to proceed uniformly in all directions, so that a biaxial stress is established in the plane of the film, perpendicular and parallel to the original stress axis. The curvature produced by differential swelling along the length of the film is also complicated by the necessity for overcoming permanent set distortion before the reverse curvature occurs. Any error in calculating the permanent set will be transferred to these measurements.

Therefore it is convenient to expose another sample of the same material at its normal length, so the curvature of the swollen sample can be more readily obtained from the radius of curvature of the swollen sample.

In this case the swollen length of the substrate layer is obtained from measurements on unexposed samples and the length of the degraded layer is calculated from the same e_0 L measurements. This treatment of the data also disregards the effect of tensile or compressive stress upon the swelling characteristics of the film.

When L_s, the length of the exposed layer, and L_u, the length of the substrate, are obtained, the ratio $(L_u/L_e)^3$ should be equal to the ratio of cross-link density in the degraded and undegraded layers. This calculation involves so many assumptions that it is reassuring to find approximately 25% agreement with gravimetric swelling measurements.

The swelling measurements give the cross-link density in the degraded layer and therefore offer a method for approximating E_1, the modulus of elasticity of the degraded layer, a quantity required in our initial calculation of permanent set.

In practice, it has been difficult to apply these equations accurately, and our data must be considered at best only semi-quantitative. The measurement of the thickness of the degraded layer is subject to extreme uncertainty. At times, and for reasons only poorly understood, the surface cannot be induced to develop a crack pattern or the cracks cannot be replicated accurately. It is particularly disconcerting when the gravimetric swelling measurements, fitted to a two-ply model, show incomplete swelling of even the substrate and absolutely no swelling of the surface, which would correspond to essentially infinite cross-linking of the surface.

We have therefore adopted a procedure for characterization which is less rigorous mathematically but which seems capable of ranking elastomers consistently in order of stability. The samples are weighed before and after exposure to determine the amount of volatilization. They are then extracted to remove benzene solubles. The sum of the volatiles and extractibles is compared to the total extractibles of an unirradiated sample. This comparison is made according to the hypothesis that the volatiles, being small molecules, would have been soluble in benzene also. The assumption is that they were originally present as small molecules, rather than that they were produced in a chain scission reaction during irradiation. In practice, under the influence of ultraviolet light we find that the volatiles and extractibles together are less than the extractibles of an unexposed film. This suggests that the principal process is one of further polymerization rather than chain scission.

Without adequate knowledge of the depth of the degraded layer, it is difficult to estimate the extent of cross-linking in the surface. Therefore our swelling measurements are averaged over the whole sample. We do find, for example, that samples which exhibit the greatest decrease in swelling after irradiation also show

the smallest radius of curvature for samples irradiated in tension (i.e., large permanent set) and the smallest radius of curvature for swollen irradiated samples. All this is consistent with the notion that the principal reaction is cross-linking rather than chain scission. This conclusion is not startling; it was predicted many years ago by Bateman (2) and more recently by Florin and Wall (3), as well as by our own group. In a medium of high internal viscosity, only very small radicals can diffuse away from the site of homolytic cleavage rapidly enough to escape recombination. Larger radicals, such as those formed by scission of the primary chain, cannot escape (the cage effect) and therefore recombine with the evolution of heat. Residual radicals, left when a hydrogen atom dissociates from the molecule, may be somewhat mobile via chain transfer, but their ultimate fate seems to be recombination with other radicals, resulting in a new cross-link. These reactions are indicated below.

$$
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C-C-R} \\
| \ | \\
\text{H H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C -C-R} \\
\cdot \ | \\
\text{H}
\end{array}
+ \ \text{H·}
$$

$$
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C-C-R} \\
| \ | \\
\text{H H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{H} \\
| \\
\text{R-C·} \\
| \\
\text{H}
\end{array}
+
\begin{array}{c}
\text{H} \\
| \\
\cdot\text{C-R} \\
| \\
\text{H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C-C-R} \\
| \ | \\
\text{H H}
\end{array}
+ \ \Delta
$$

$$
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C-C-R} \\
\cdot \ | \\
\text{H}
\end{array}
+
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R'-C-C-R'} \\
| \ | \\
\text{H H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C-C-R} \\
| \ | \\
\text{H H}
\end{array}
+
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R'-C-C-R'} \\
\cdot \ | \\
\text{H}
\end{array}
$$

$$
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R-C-C-R} \\
\cdot \ | \\
\text{H}
\end{array}
+
\begin{array}{c}
\text{H H} \\
| \ | \\
\text{R'-C-C-R'} \\
\cdot \ | \\
\text{H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{R} \ \ \ \ \ \text{R'} \\
| \ \ \ \ \ \ | \\
\text{H-C———C-H} \\
| \ \ \ \ \ \ | \\
\text{H-C-H} \ \ \text{H-C-H} \\
| \ \ \ \ \ \ | \\
\text{R} \ \ \ \ \ \ \text{R'}
\end{array}
$$
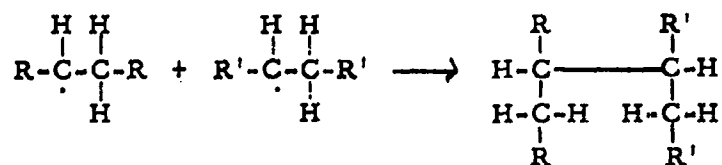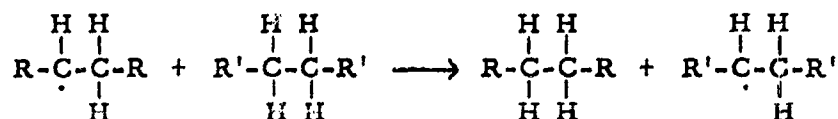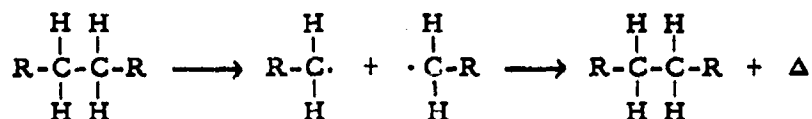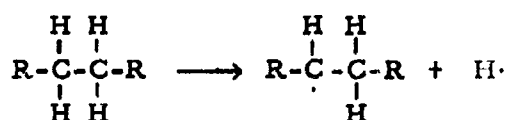
This is in sharp contrast to the photolysis reaction in oxygen or air, where the radicals combine primarily with oxygen to form peroxy radicals. These in turn decompose in various ways to give oxygenated degradation products in a chain reaction. In contrast, the reaction sequence described above is not a chain reaction, and each new cross-link requires two effective scissions. Therefore, it is not surprising that the rate of reaction in the absence of oxygen is very much slower. This also suggests the extreme precaution necessary to exclude oxygen from the system, since even at very low pressures of oxygen the oxidation reaction

will proceed more rapidly. Frequently the presence of minute amounts of oxygen in the system are first observed in the volatile degradation products. It seems probable that the difference sometimes reported in the photolysis of polymers in vacuo and in the presence of an inert gas (in the absence of a demonstrable reaction with the inert gas) is caused by oxygen contamination.

Order-of-magnitude calculations show that at approximately 3x solar intensity an oxygen pressure of 10^{-5} mm is required to react with all the radicals which could be photochemically generated, assuming a quantum yield of unity. This is therefore the minimum oxygen pressure which could produce substantial oxidation; the actual value may be several orders of magnitude higher.

To illustrate the application of these techniques to actual samples we will now consider some typical data. Our first experimental materials are shown in Table 1. These are typical elastomer formulations, which contain almost no volatiles. Figure 6 shows photomicrographs of some of these materials after irradiation. Typical experimental data for Series I are given in Table 2. The negative radius of curvature of the last group of samples after swelling is not significant, since no swelling took place, as shown by the small weight imbibed.

It has been pointed out that the swelling of a filled elastomer depends upon the filler as well as the extent of cross-linking and that volume changes upon swelling must be corrected for the volume of carbon black or other added materials. It was therefore decided that further work should involve pure gum stocks rather than complex rubber formulations. It was hoped also that the degradation of these materials might be more nearly homogeneous, thus making possible a simpler and more accurate characterization of the photolysis reaction. The composition of this series of materials is given in Table 3. The exposure of these materials to ultraviolet and vacuum produces much more severe changes than are observed in the pigmented samples, as shown in Tables 4, 5, and 6. However, the reaction is still not homogeneous through the film, as evidenced by the curvature of the samples. It is possible, however, to correlate the severity of the curvature, both swollen and unswollen, with the change in gravimetric swelling. Ranking the materials in order of decreasing stability, the following order is obtained: butyl > saturated ethylene propylene > unsaturated ethylene propylene rubber > Hycar > smoked sheet > FRS1502, a styrene-butadiene type. Viton A is not included because its special characteristics make comparison difficult; it is, however, quite stable.

Since it has been shown that the photolysis reaction is largely confined to the irradiated surface, the technique of attenuated total reflectance (ATR) seems potentially applicable (4). In brief, this technique takes advantage of the fact that when two materials

Table 1

FIRST EXPERIMENTAL SAMPLES

| Elastomer | Composition | | Cure |
	Component	Parts	
Neoprene No. 403411	Neoprene W Magnesium oxide Zinc oxide HMF black NA-22	100 2 5 80 0.5	30 min at 307°F
Natural Rubber No. 401700	Smoked sheets Stearic acid Zinc oxide Sulfur MBT PBNA EPC black	100 1 1 3 1 1 50	40 min at 284°F
SBR No. 409549	Philprene 1500 FEF black Zinc oxide Stearic acid Agerite Alba Altax Sulfur Methyl Zimate	100 80 5 2 1 1.5 2 0.1	15 min at 307°F
Carboxy-Nitrile No. 417365	Hycar 1072 Stearic acid FEF black Dicumyl peroxide Zinc oxide	100 1 40 5 5	15 min at 320°F
Urethane No. 404293	Adiprene C HAF black MBTS MBT Sulfur RCD-2098	100 30 4 1 0.75 0.35	60 min at 287°F
Polyacrylic No. 427607	Hycar 4021 HFM black Stearic acid Zinc oxide Triethylene- tetramine	100 40 1 10 1.5	30 min at 310°F

Miller

Table 1 (cont.)

| Elastomer | Composition | | Cure |
	Component	Parts	
Nitrile No. 417366	Hycar 1042 Zinc oxide FEF black Methyl Tuads Sulfur Stearic acid	100 5 75 3 0.2 1	15 min at 320°F
Silicone No. 429809	Silastic SE 555-U	100	10 min at 250°F Postcure 24 hr at 400°F
Hypalon No. 408622	Hypalon 40 Litharge HAF black MBTS Tetrone A	100 25 60 0.5 2	30 min at 307°F
Fluorosilicone No. 429808	Silastic LS-63	100	10 min at 250°F Postcure 24 hr at 400°F
Butyl No. 409724	Butyl 325 SRF black Zinc oxide Stearic acid Red lead GMF	100 90 5 2 10 2	20 min at 320°F
Fluoroelastomer No. 429120	Viton A MT black Magnesium oxide Diak No. 2	100 25 20 1	30 min at 320°F Postcure 24 hr at 400°F
Fluoroelastomer No. 429121	Viton B MT black Magnesium oxide Diak No. 2	100 25 20 2	30 min at 320°F Postcure 24 hr at 400°F

Sample 401700   Sample 404293   Sample 408622

Sample 409549   Sample 417365   Sample 417366

Sample 427607   Sample 429124   Sample 429809
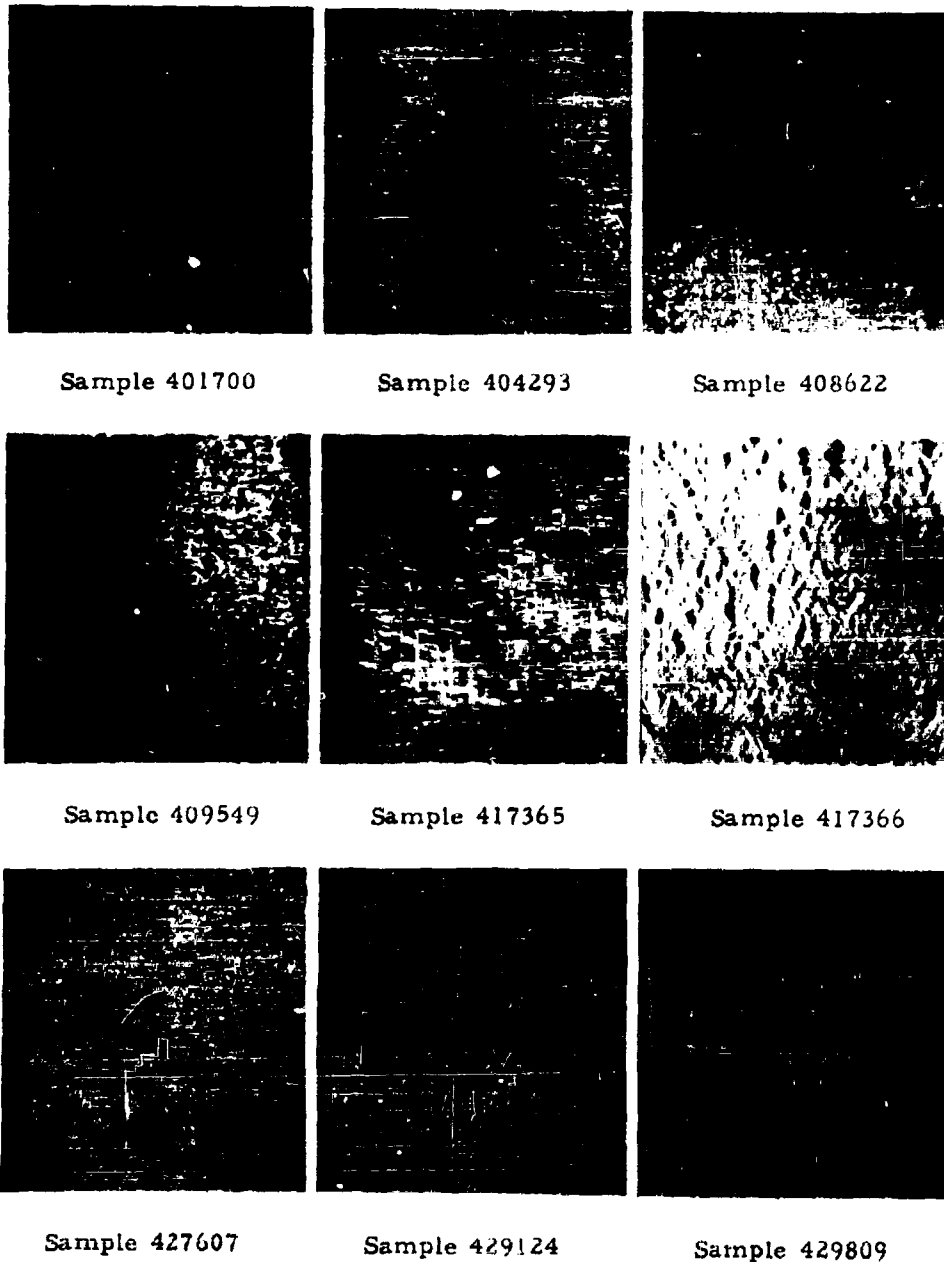
Fig. 6. Photomicrographs of Degraded Surfaces
of Elastomers after 100 hr of Irradiation (0. 1 mm = 1 cm)

Table 2

EXPERIMENTAL DATA FOR SERIES 1

Sample No.	Wt. Changes due to Irradiation, mg			Swollen Wt., g	Extracted Wt., g	Wt. Imibibed, g		Radius of Curvature, cm	
	Before	After	Loss			Exposed Sample	Control Sample	Before Swelling	After Swelling
401700	112.8	111.1	1.7	0.2568	0.0906	0.1662	0.283	0.60	+1.8
408622	167.1	166.1	1.0	0.1997	0.1071	0.0926	0.1086	1.13	No curl
409549	130.7	128.8	1.9	0.2224	0.0994	0.1230	0.1994	0.82	No curl
409724	150.9	151.9	-1.0	0.1762	0.1197	0.0565	0.0635	No curl	-
417365	156.9	154.1	2.8	0.3379	0.1127	0.2252	0.271	1.49	+2.39
417366	141.5	137.8	3.7	0.2864	0.1088	0.1776	0.260	0.91	No curl
427607	145.0	144.4	0.6	0.3489	0.1091	0.2398	0.304	1.52	No curl
									twist
429120	196.0	195.7	0.3	0.1703	0.1654	0.0049	0.00615	0.75	-0.56
429121	262.8	262.5	0.3	0.2192	0.2172	0.0020	0.00428	1.55	-0.99
429808	232.5	230.8	1.7	0.1834	0.1754	0.0080	0.00912	0.11	-0.14
404293	124.9	Broke							

Table 3

ELASTOMER COMPOSITIONS SERIES

No.	Cure	Components	Parts
I	45 min at 280°F	Smoked sheets	100
		Stearic acid	1
		Zinc oxide	5
		Methyl Tuads	3
		Altax	0.5
II	30 min at 318°F	Butyl 268	100
		Stearic acid	2
		Zinc oxide	5
		Methyl Tuads	1.5
		Altax	1
III	30 min at 318°F postcured 1 hr at 300°F and 24 hr at 350°F	Viton A	100
		Magnesium oxide	5
		Diak No. 2	1.25
IV	30 min at 300°F	FRS 1502	100
		Zinc oxide	5
		Stearic acid	2
		Methyl Tuads	3
		Altax	1.5
V	30 min at 318°F	ECD-330 (unsaturated ethylene propylene rubber)	100
		Tetrone A	4
		Altax	1
		Zinc oxide	5
		Stearic acid	0.5

Table 3 (cont.)

No.	Cure	Components	Parts
VI	30 min at 318°F	ECD-330	100
		Di Cup	3.5
VII	30 min at 300°F	Hycar 1042	100
		Zinc oxide	5
		Stearic acid	1
		Methyl Tuads	3.5
VIII	30 min at 318°F	EPR 60(saturated ethylene-propylene rubber)	100
		Di Cup	3
		Sulfur	0.03
IA	45 min at 280°F	Smoked sheets	100
		Stearic acid	1
		Zinc oxide	5
		Methyl Tuads	3
		Altax	0.5
		SRF black	5
IIA	30 min at 318°F	Butyl 268	100
		Stearic acid	2
		Zinc oxide	5
		Methyl Tuads	1.5
		Altax	1
		SRF black	5

Table 4

WEIGHT CHANGES IN ELASTOMERS
AFTER IRRADIATION, EXTRACTION, AND SWELLING

Elastomer No.	Initial Wt., g W_o	Wt. after Irradiation, g W_a	Difference, g $W_b = W_o - W_a$	Volatile, % W_b / W_o
I	0.1825	0.1802	0.0023	0.0126
IA	0.1765	0.1728	0.0037	0.0210
II	0.1948	0.1935	0.0013	0.0067
IIA	0.1563	0.1541	0.0022	0.0141
III	0.4121	0.4121	0.0000	0.0000
IV	0.2196	0.2172	0.0024	0.0109
V	0.2898	0.2821	0.0077	0.0266
VI	0.2093	0.2057	0.0036	0.0172
VII	0.2943	0.2912	0.0031	0.0105
VIII	0.1838	0.1800	0.0038	0.0207

Table 4 (cont.)

Elastomer No.	Extracted Wt., g[a] W_1	Difference, g $W_2 = W_o - W_1$	Soluble, % $R_1 = W_2/W_o$
I	0.1767	0.0058	3.18
IA	0.1698	0.0067	3.80
II	0.1815	0.0133	6.83
IIA	0.1462	0.0101	6.46
III	0.4180	-0.0059	-1.43
IV	0.2069	0.0127	5.78
V	0.2709	0.0189	6.52
VI	0.1986	0.0107	5.11
VII	0.2868	0.0075	2.55
VIII	0.1538	0.0299	16.27

Table 4 (cont.)

Elastomer No.	Wt. before Swelling, g[b] W'_1	Swollen Wt., g[c] W_3	Avg. Dev., g[d] ΔW_3	Difference, g $W_4 = W_3 - W'_1$	Ratio $R_2 = W_3/W'_1$	Error, % $\Delta W_3/W_3 \times 100\%$
I	0.1332	0.6318	0.93	0.4986	4.7432	0.15
IA	0.1352	0.6752	0.60	0.5400	4.9941	0.09
II	0.1498	0.2910	0.40	0.1412	1.9426	0.14
IIA	0.1223	0.2340	0.32	0.1117	1.9133	0.14
III	0.3362	0.3434	0.08	0.0072	1.0214	0.02
IV	0.1531	0.7039	1.70	0.5508	4.5976	0.24
V	0.2168	0.5216	0.16	0.3048	2.4059	0.03
VI	0.1561	0.3803	0.37	0.2242	2.4363	0.10
VII	0.2180	1.4698	0.81	1.2518	6.7422	0.06
VIII	0.1184	0.2935	0.27	0.1751	2.4789	0.09

[a]Extracted 1/2 hr in benzene. Dried 40 hr.

[b]Samples cut to 2-in. length before swelling.

[c]Soaked in 1-methylnaphthalene 5 days.

[d]Six or more weighings were made of each sample, except IV, which crumbled.

Table 5

WEIGHT CHANGES IN UNIRRADIATED ELASTOMERS
AFTER EXTRACTION AND SWELLING

Elastomer No.	Initial Wt., g W_o	Extracted Wt., g[a] W_1	Difference, g $W_2 = W_o - W_1$	Soluble, % $R_1 = W_2/W_o$
I	0.2498	0.2383	0.0115	4.60
IA[b]	0.1948	0.1862	0.0086	4.42
II	0.2201	0.2055	0.0146	6.63
IIA	0.1965	0.1834	0.0131	6.67
III[b]	0.4789	0.4816c	-0.0027	-0.56
IV	0.2559	0.2294	0.0265	10.36
V	0.3404	0.3131	0.0273	8.02
VI	0.2597	0.2452	0.0145	5.58
VII	0.3434	0.3244	0.0190	5.53
VIII	0.2361	0.2007	0.0354	14.99

Table 5 (cont.)

Elastomer No.	Swollen Wt., g[d] W_3	Avg. Dev., g ΔW_3	Difference, g $W_4 = W_3 - W_1$	Ratio $R_2 = W_3/W_0$	Error, % $\Delta W_3/W_3 \times 100\%$
I	1.3891	0.94	1.1508	5.8292	0.07
IA	1.0039	0.80	0.8177	5.3915	0.08
II	0.4003	0.76	0.1948	1.9479	0.19
IIA	0.3518	0.53	0.1684	1.9182	0.15
III[b]	0.4988	0.11	0.0172	1.0357	0.02
IV	1.4142	0.90	1.1848	6.1648	0.06
V	0.7807	0.80	0.4676	2.4935	0.10
VI	0.6275	0.50	0.3823	2.5591	0.08
VII	2.4605	0.90	2.1361	7.5848	0.04
VIII	0.5065	0.40	0.3058	2.5237	0.09

[a]Extracted 1/2 hr in benzene. Dried 40 hr.

[b]These two samples were put through the cycle out of phase with the rest. Thus, the times listed in the first and fourth footnotes are only approximate for these samples.

[c]The increase in weight was probably due to residual benzene. Even though the sample was dried an extra day, the weight was still high.

[d]Swollen in α-methylnaphthalene 5 days. Weights listed are the average of seven or more weighings.

Table 6

RADIUS-OF-CURVATURE MEASUREMENTS[a]

Sample No.	Swollen Radius (Differential Swelling)		Extracted Radius (Permanent Set)		Comment on Extracted Radius
I	+ SC	0.11 in.	- LC	0.13 in.	
IA	+ SC	0.18	- LC	0.08	
II	+ Sp	0.26	+ LC	0.26	J shape
IIA	- LC	0.30			Curly
III	- LC	0.46	- LC	0.48	
IV	+ SC	0.12	- LC	0.06	Crumbly
V	+ LC	1.10	- LC	0.35	
VI	+ SC	0.38	- LC	0.19	
VII	+ LC	0.28	- LC	0.14	Twisted
VIII[b]	- SC	0.45			
	+ LC	0.23			

[a] + means curled toward light
- means curled away from light
SC means short curl
LC means long curl
Sp means spiral--a long curl that does not close upon itself but tends to form a long tube

[b] Sample VIII was SC at one place and LC at another.

are in optical contact with one another and a beam of radiation is totally reflected internally from the faces in contact there will be a transfer of energy between the two materials roughly proportional to the ratio of the indices of refraction. Since the refractive index of a material changes rapidly at wavelengths of absorption, a plot of this energy transfer versus wavelength closely resembles a conventional absorption spectrum. The ATR measurements are sensitive only to the sample composition in the top 5 μ of the thickness. This overcomes a prime difficulty of standard transmission measurements, i.e., the degradation is essentially a surface reaction and the unchanged bulk of the material "dilutes" the changes produced by the photolysis.

In comparison with measurements of mechanical properties, such a technique is mathematically less elegant and probably would afford at best only a semiquantitative interpretation. In practice it has not been possible to apply these aesthetically satisfying equations to much more than an order of magnitude. Moreover, an indication of the site and chemical nature of the photolysis reaction should be of real advantage in designing more stable structures for elastomers.

An optical diagram of the apparatus is given in Fig. 7. The two positions of the mirrors indicate the extreme positions of the reflecting elements, which move synchronously to give a predetermined angle of reflection from the coated surface. This angle of incidence depends upon the nature of the optical material used at D and the nature of the coating whose spectrum is to be obtained. Much of our work during the past month has been devoted to the systematic study of these variables. Figure 8 shows the transmission spectrum of nitrocellulose and the ATR spectrum of the same material at various angles of incidence. The similarity of the ATR spectrum and the transmission spectrum is apparent; equally obvious is the marked effect of the angle of incidence on the sharpness of the ATR spectrum.

These spectra were obtained by depositing solutions on the back of corduroy-faced pressed silver chloride plates, which act as a series of prisms but which can be made by pressing and are therefore much less expensive than the massive prism shown in the diagram. However, this arrangement proved insufficiently rigid for solid samples, where considerable clamping pressures are required to obtain optical contact between the prism material and the specimen. Attempts to get contact by wetting our elastomer samples with a thin film of mineral oil were moderately satisfactory on the unirradiated surfaces, but the irradiated surfaces seemed spongy and gave visibly poor contact with correspondingly poor spectra. Solid prisms which will permit the proper clamping of samples have been obtained, but data are insufficient to report at this time.
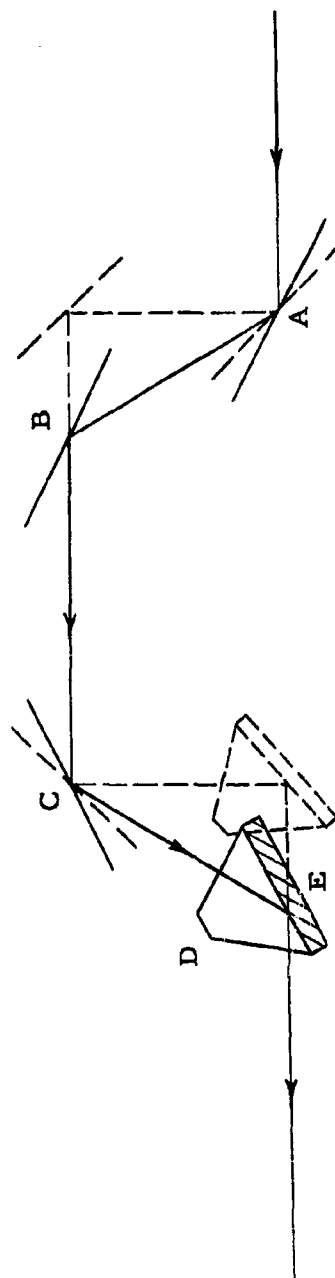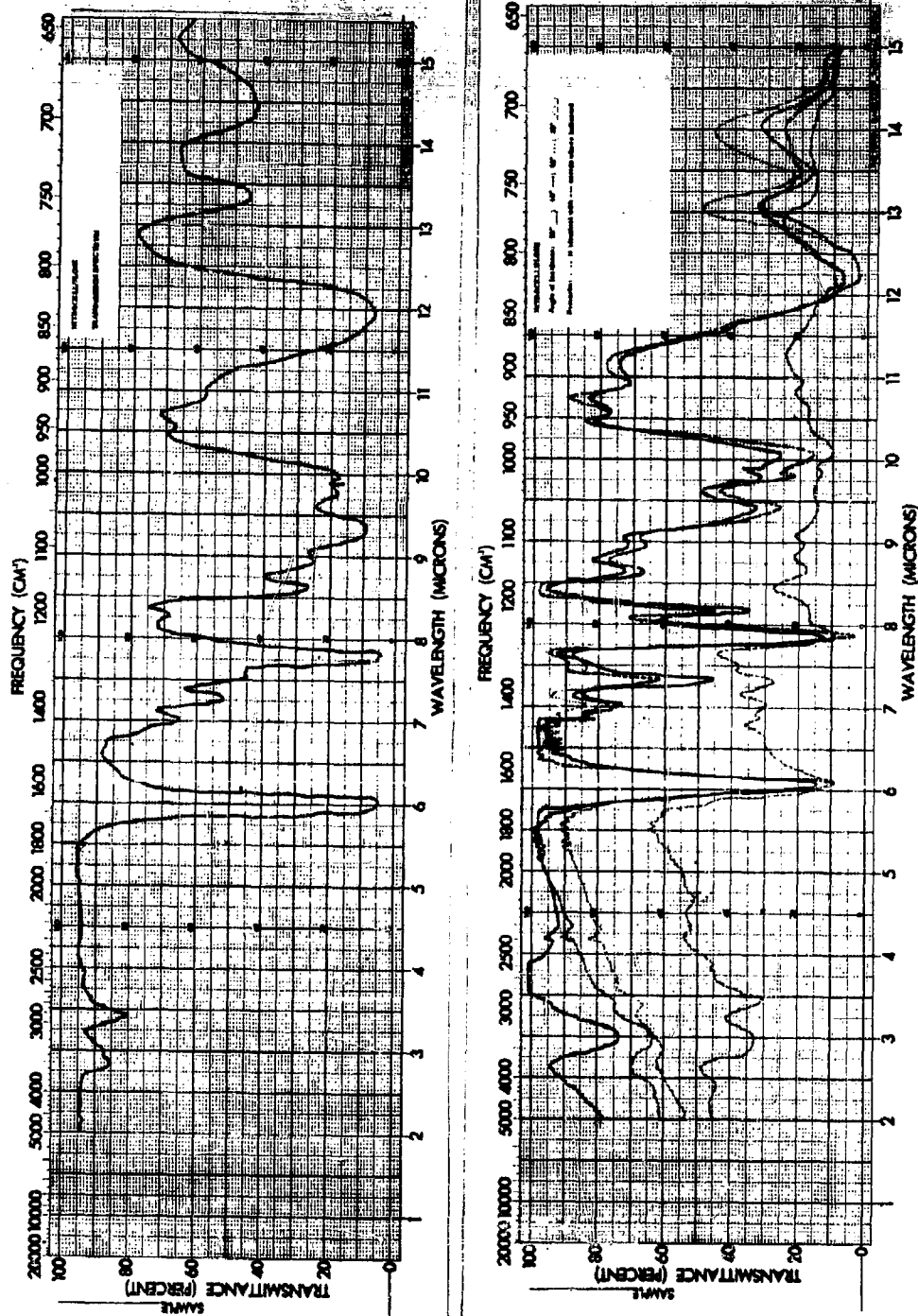
Fig. 7. Attenuated Total Reflectance

Fig. 8. Comparison of ATR and Transmission Spectra

The thermal stability of these materials has been investigated at moderate temperatures, not in excess of 200°F, a range that might be anticipated in space vehicles. Most of th work which has been done has been at higher temperatures. It frequently has been carried out in the presence of oxygen.

It is difficult to predict the effect of temperature on the photolysis reaction. In principle, the photochemical reaction should be temperature independent, but this is true only for the initial photochemical event. In complex systems, such as we are discussing here, the temperature may indeed be an important factor. Bateman (2) has found dehydrogenative cross-linking below 150°C, but above this temperature, isoprene appears in the volatile products. He also finds a small activation energy (1.5 kcal) for noncondensible gas formation.

In our own work, the use of temperatures in excess of 200°F is somewhat unrealistic, since most space craft, whether manned or unmanned, must be maintained at lower temperatures to safeguard the instruments and occupants. For most of our work we permit the temperatures to equilibrate without external cooling of the samples. At 3 to 4x solar intensity the sample temperatures do not exceed 200°F. On occasion, additional heat has been supplied by General Electric quartz incandescent lamps. In such cases, we find a slightly increased rate of evolution of volatiles and perhaps some slight indication of chain scission. Experiments in which the samples are heated at these temperatures in vacuum show no appreciable degradation beyond the slight evolution of volatiles. This does not exceed the amount of soluble material, which is considered at least potentially volatile.

In summary, our study of the vacuum photolysis of various elastomers has shown that the principal reaction is cross-linking rather than chain scission, that the reaction occurs on the irradiated surface rather than through the bulk of the sample, and that various elastomers differ one from another in their stability in the aerospace environment, although all are subtantially more stable than they would be in an oxidizing atmosphere.

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ELASTOMERS FOR NEUTRON SHIELDING

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Introduction

It is likely that future battlefields will be characterized by both conventional and atomic weapons. These weapons produce effects which differ both in degree and kind. The destructive action of both is due mainly to blast or shock but atomic blasts can be many thousands (or millions) of times more powerful than the largest conventional detonations. In addition, the atomic or nuclear weapons yield significant amounts of thermal radiation, initial nuclear radiation, and residual nuclear radiation. The proportion of each of these effects in a typical air burst of a fission weapon at an altitude below 100,000 feet is approximately as indicated in Fig. 1.[1] For reasons which will become clearer as we proceed, the present discussion is concerned only with the initial nuclear radiation - the smallest portion of the energy liberated in the explosion. This is defined as the radiation emitted within one minute of the detonation. This somewhat arbitrary time is based on the fact that, due to attenuation by the air, radiation received at a distance of two miles from the source is negligible and it takes roughly a minute for the radioactive cloud to reach two miles. This initial radiation consists of gamma rays, neutrons, beta particles, and a small proportion of alpha particles. Because of their short ranges, alpha and beta particles can be ignored. However, both the gamma rays and neutrons can travel considerable distances through air and produce deadly effects on exposed personnel. This radiation becomes important only in the case of tactical atomic weapons or those having energy yields under 10 KT since in the larger bombs the area of total destruction due to blast and flame overlaps the area in which radiation is a hazard. For example, beyond
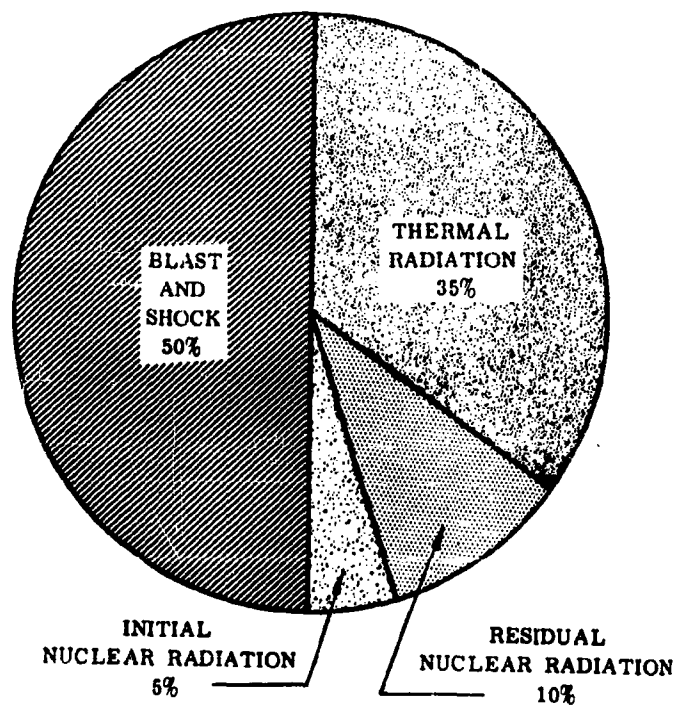
ENERGY DISTRIBUTION FOR FISSION WEAPON
AT AN ALTITUDE BELOW 100,000 FT.

FIG. I

3895

about 1-1/4 miles the initial nuclear radiation from a 20 KT air burst would not cause observable injury even without protective shielding. However, exposure to thermal radiation at this distance could produce serious skin burns. On the other hand, when the energy of the nuclear explosion is relatively small, e.g. a KT or less, the initial nuclear radiation has the greater effective range.[2]

A decided tactical advantage would accrue to radiation shielded combatants who could maneuver at will in those battlefield areas which would be subjected to lethal radiation but which would be outside the area of destructive effects caused by blast and flame. Such personnel could also utilize their own nuclear devices at a closer and more effective range. An approximate representation of the situation which would prevail in the case of a 10 KT detonation is depicted in Fig. 2. Since the present discussion is concerned primarily with ballistically armored vechicles, shielding against neutron radiation is of paramount importance. This is due to the long range, high energy, and penetrating power of these particles. Gamma rays having long range and high energies also result from the blast but these are largely attenuated by the ballistic armor. The gamma radiation which must be guarded against is that resulting from neutron-gamma reactions (n, γ) resulting from radiative capture by components of the atmosphere, ground, and elements contained in the shield itself.

Requirements for Radiological Shield

A satisfactory radiological shielding material must possess two main characteristics viz (1) high radiation attenuation and (2) processability and adaptability to the particular configuration and end use. The extent to which radiation is attenuated depends upon the nature of the radiation, the nature of the shielding material(s) and on their relative thickness and arrangement. The efficiency of a material for shielding gamma radiation is directly proportional to its density. Consequently, the dense ballistic armor required against conventional weapons will serve to largely attenuate the gamma radiation (except for the secondary gammas resulting from the (n, γ) reactions as previously mentioned). The attenuation of high energy neutrons, on the other hand, involves two principal steps viz. (1) thermalization or conversion of the fast neutrons to thermal neutrons which have about the same kinetic energy as the surrounding gas molecules (.025-.038ev) and (2) capture, which involves the reaction of the thermal neutron with another
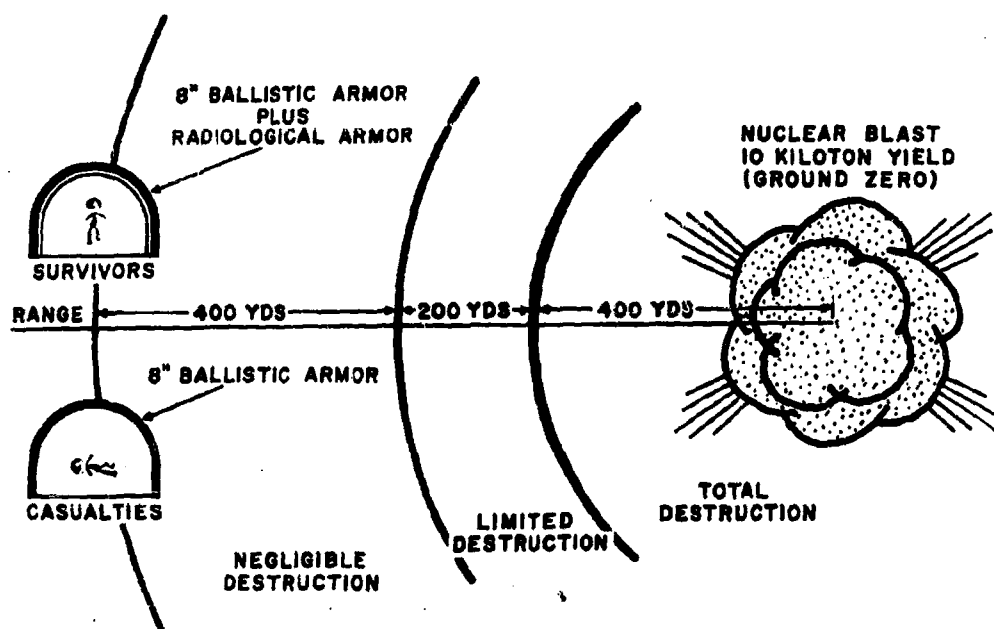
PROTECTION AFFORDED PERSONNEL BY RADIOLOGICAL SHIELDING

FIG. 2   3889

element. The efficiency with which an element will slow down neutrons depends in part upon the energy of the neutrons. Fast neutrons with energies in excess of about 1 Mev will be slowed by inelastic collisions with elements of high mass numbers such as the iron used for ballistic shielding. When their energies have been reduced to about 0.1 Mev, the so-called elastic scattering by light elements is most effective in reducing these energies to the thermal range. Since hydrogen is the element nearest in mass to the neutron, collision of these two particles results in a maximum transfer of energy.[3] Consequently, a maximum hydrogen concentration per unit volume (hydrogen density) is desirable in a neutron shield. The second step involved in neutron attenuation, that of reaction with another element, depends upon the capture cross section of the element. This cross section is a measure of the probability of reaction between an atom of a given element and a neutron upon collision. It varies with the energy of the neutron and with the element or isotope chosen. In many cases when an element reacts with a thermal neutron, lethal high energy radiation is emitted. The element chosen for this step must, therefor, have both a high capture cross section for thermal neutrons and the products which result from neutron capture must be innocuous. Some information which is useful in the selection of materials for neutron attenuation is furnished in Table I. It is immediately evident from inspection of this table why materials having a high concentration of hydrogen are preferred for thermalization. For neutron capture, as already mentioned, an element having high thermal cross section which yields low energy products upon reaction is desired. Among the elements listed, boron appears to possess this combination to the optimum degree. Lithium would probably be a second choice. Elements such as gadolinium and cadmium have very attractive cross sections but would be of little use since they emit hard gammas which would be as much a hazard as the neutrons which we are attempting to attenuate. Another important point which is brought out in this table is that thermalization efficiency varies only slightly with neutron energy. This could mean that very high energy neutrons resulting from a neutron bomb or other source might be satisfactorily attenuated by use of only slightly greater shield thicknesses.

Materials For Radiological Shielding

In view of the above, it is apparent why borated high density polyethylene is the shielding material of choice in the design of stationery reactors or those in which no special fabrication problems exist. It has high

TABLE I

THERMALIZATION AND CAPTURE PROPERTIES OF NUCLEI

Element	Collisions to Thermalize			Thermal Cross Section – Barns	Highest Energy γ Resulting From Capture – Mev
	1 Mev	3 Mev	6 Mev		
H	18	19	19	.33	2.2
D	25			.00057	
Li	65	69	72	70	0.1
B	102	108	112	715	.48
C	111	118	122	.0045	4.9
N	129	137	142	0.1	10.8
O	146	155	161	.0002	6
Cd				3,300	9
Fe	496	527	547	2.5	10
Gd				38,000	7.8
Pb				.17	7.4

hydrogen density for optimum thermalization, boron for
capture, is readily available at reasonable cost, stable
and fairly easy to process. However, this material has
several drawbacks when its use is contemplated for a
light weight mobile shield for use with armored vehicles.
In the latter instance, probably the most desirable solu-
tion would be to have a material which could be cast at
room temperature between the inner and outer shells of
the armor and cured in situ to produce a component having
properties as listed in Table II. Polyethylene would not
be well suited in such an application because of shrink-
age problems and presence of voids when cast.[4] The use
of polyethylene slabs would be extremely difficult due to
the configuration involved and shrinkage problems asso-
ciated with operation of the vehicle under extremes of
climatic conditions.

For the purpose of developing a satisfactory
shielding component, a two phase program has been
initiated at Rock Island Arsenal to make available a
high hydrogen density elastomeric composition which could
be cast and cured at room temperature and have properties
as shown in Table II.

Phase I

The first phase is a comparatively short range
project directed at making a shielding material avail-
able in the near future. It consists primarily of the
modification of currently available liquid polymers which
might have promise for this application. Phase two is a
longer range program concerned with the synthesis of a
liquid, boron modified, elastomer specifically designed
for this application.

The possession of high hydrogen density was
considered of paramount importance in the selection of
polymers and compounding ingredients to be evaluated for
the first phase. The hydrogen densities of some of the
polymers and materials of potential use in shielding are
shown in Table III. High density polyethylene was used
as a reference standard due to its widespread use and
very satisfactory hydrogen density. It was the ultimate
goal of this project to match the hydrogen density of
this material in an elastomeric composition having more
suitable processing and fabricating properties. With
liquid polymers it is frequently possible to signifi-
cantly increase the hydrogen densities of the systems
by incorporating a filler or curative of greater hydrogen
density. Should such additives also contain boron an
additional advantage would be obtained. Our interest in

TABLE II
DESIRABLE PROPERTIES FOR NEUTRON SHIELD

1. HIGHEST POSSIBLE HYDROGEN DENSITY.

2. COMPATIBLE WITH AN ELEMENT SUCH AS BORON WHICH HAS HIGH THERMAL NEUTRON CROSS SECTION.

3. EASILY PROCESSED AND FABRICATED — CASTABLE AND CURABLE AT ROOM TEMPERATURE, HOMOGENEOUS, VOID FREE, NON SETTLING.

4. HAVE ENVIRONMENTAL STABILITY.

5. BE COMPOSED OF NON TOXIC MATERIALS.

6. NON BRITTLE UPON IMPACT AT $-67°F$.

7. REASONABLE AVAILABILITY AND COST.

3605

TABLE III

DESCRIPTION OF SOME POTENTIAL SHIELDING MATERIALS

Material	H Density (Sp.Gr.X%H)	Physical State (R.T.)	Remarks
Tetramethyl ammonium borohydride	.147	Solid	May be useful as boron component of shield.
Polyethylene(High Density)	.137	Solid	V.G. for reactor shielding; Ex. H. Density.
Polyethylene (Low Density)	.131	"	V.G. for reactor shielding; Good H density.
Paraffins	.129-.133	"	May be useful as shielding component.
Butyl Rubber	.131	"	May be useful as base polymer in shield.
Polyisobutylene	.131	"	May be useful as additive in shield
Polypropylene	.129	"	" " " " "
Lithium borohydride	.126	"	" " " " "
Polybutene	.125	Liquid	" " " " "
Sodium Borohydride	.114	Solid	May be useful as boron component of shield. "
Tridecyl Borate	.113	Liquid	" " "
Proprietary Shielding Elastomer	.113	Vis.Liquid	Poor castability; Material has poor strength resembling "art gum." 5.
Water	.111	Liquid	May be useful as shielding component.
DPR(Cis-1,4 polyisoprene)	.111	"	May be useful as base polymer in shield.
DPR (Natural Rubber)	.111	"	" " " " "

239

TABLE III (CONT.)

Material	H Density (Sp.Gr.X%H)	Physical State (R.T.)	Remarks
Decarborane	.108	Solid	May be useful as boron component of shield.
Fuel Oil	.106	Liquid	May be useful as shielding component.
Lithium Hydride	.103	Solid	" " "
Polyallyl glycidyl ether	.099	Liquid	" " "
Polymethyl methacrylate	.096	Solid	May be useful where transparency is needed.
Polybutadiene	.095	Liquid	May be useful as base polymer for shield.
Hydrogen (Liq.) – 253°C.	.071	"	Impractical to use; H density not very good.

tetramethyl ammonium borohydride stemmed from such considerations and since it was not readily available it was synthesized as described by Banus et al.[6] Liquid hydrogen is included in Table III only as a matter of interest since it would not be a practical shielding material and has poor hydrogen density due to low specific gravity. The resistance of the polymers to radiation damage was not considered a problem since anticipated total dosages would fall well below the damage thresholds of even the least radiation resistant elastomers. It is important in the selection of curatives, polymers, and other compounding ingredients that elements which have objectionable (n,γ) interactions be kept at an absolute minimum. These include, among others, chlorine, nitrogen, sulfur, silicon, manganese, and sodium.

A summary covering most of the polymeric materials investigated under this phase of the work is presented in Table IV. Details pertaining to methods of polymer preparation or modification compounding, curing, testing etc. will not be discussed here since they have been dealt with elsewhere.[7,8] The depolymerized butyl rubber was prepared by chemical breakdown using either peroxides or mercaptans, by controlled thermal degradation or by subjecting the elastomer to gamma radiation. In the latter instance, a product readily pourable at room temperature could be obtained at dose levels of approximately 250 megarads. This was the most satisfactory method found for preparing liquid butyl. However, due to its low degree of unsaturation, room temperature curing was not successful. The carboxy terminated liquid polybutadiene showed more promise for room temperature curing than the polymer having carboxyl groups in pendant positions.

Other systems examined included various greases prepared from stearates and polybutenes, viscoelastic gels based on combinations of high density polyethylene and polybutenes, hot melts of polyisobutylene with emulsifiable polyethylene, emulsions of butyl latex with polyethylene, solutions of butyl rubber in kerosene or polybutenes, a boron modified acrylic acid terpolymer[9], and a carboxy modified polybutadiene containing 6% boron in the form of an alkyl carborane.[10]

Among the compositions thus far examined, two appear to offer the most promise in meeting the requirements for this application. These are shown in Table V. It should be emphasized that time did not permit complete optimization of these systems. It is quite possible that the hydrogen densities and castabilities could be

241

TABLE IV

Summary of Polymeric Materials Investigated For Castable Shield

Polymer	Cures or Modifications Examined	Castability @ R.T.	Curability @ R.T.	Reference
Butyl/Polybutene	6	Good-Excellent	Excellent	8
Carboxy(Pendant) Poly-butadiene – Epoxy Resin	14	Good-Excellent	Good	7
Depolymerized Butyl	30	Good	Poor	7,8
Depolymerized Natural and cis-polyisoprene	36	Excellent	Poor to Good	7,8
Carboxy Modified Butyl	6	Good	Poor	8
Butyl Latex	6	Excellent	Good	7
Carboxy(Pendant) Poly-butadiene	114	Excellent	Poor to Good	7,8
Carboxy(Terminal) Poly-butadiene	8	Excellent	Good	8
Polybutadiene	17	Excellent	Poor	8
Epoxy Resins	35	Good	Poor-Excellent	7,8

TABLE V

Castable Elastomeric Compositions Offering Promise For
Shielding Application

Ingredient	Parts by Weight	
	Butyl/ Polybutene/ Polyethylene	Carboxy(P)Poly- butadiene/Epoxy/ Polyethylene
Butyl Rubber (2.1-2.5% unsat.)	15	
Polybutene	85	
High Density Polyethylene (Pellets)	50	
High Density Polyethylene (Powder)	20	
Carboxy (Pendant) Polybutadiene		100
Epoxy		28
Polyethylene (Emulsifiable)		100
Aliphatic Polyamine		12
Boron	9.45	12.63
p-Quinone dioxime	4	
Lead Dioxide	4	
Triethanolamine	1.6	
Hydrogen Density	.127	.120
Castability @ R.T.	Fair	Good
Curability @ R.T.	Excellent	Excellent
Environmental Stability	Excellent	Very Good
Low Temperature Properties	Nonbrittle @ -67°F	-
Physical Strength	Fair	Fair
Boron Concentration, %	5.0	5.0

243

improved. For example, use of high density polyethylene (in place of emulsifiable) and a poly (allyl glycidyl ether) in the polybutadiene based composition would increase the hydrogen density to 0.125g/cc. Considering all factors the butyl/polybutene blend is probably the most suitable. This may be prepared by heating and stirring the butyl/polybutene mixture under an inert atmosphere at 150°C. for four hours to effect a homogeneous solution which is pourable at room temperature. Addition of the polyethylene, curatives, and 4 to 8% elemental boron (considered optimum for this application[11]) may be easily done at room temperature. The resulting mixture is about the consistency of a caulking compound and sets up to an elastic, nonflowing, slightly tacky product after about 24 hours at room temperature. The use of a compatible, stable, high boron content liquid chemical such as an alkyl carborane in place of the elemental boron would improve castability and eliminate any problem of nonhomogeniety due to settling of the boron prior to curing.

To summarize the first phase of the program, the polymers or polymer combinations listed in Table VI (in order of preference) would be considered most suited for use as bases in the preparation of a castable shielding component. This rating is based on hydrogen density and other factors of importance to the end application.

Phase II

The second phase of this program is concerned with the synthesis of a high hydrogen density, castable, vulcanizable elastomer having 4 to 8% boron chemically bound in the structure. Such an elastomer would be ideally suited to this application since it would be a single component system thereby simplifying application and eliminating the risk of nonhomogeneity. This approach may also provide the best opportunity for maximizing the hydrogen content.

A literature survey[12] covering boron polymers containing the elements carbon, hydrogen, oxygen, and boron (other elements were not included since unfavorable $(n, \checkmark)$ reactions might result if polymers containing them were used for shielding) revealed that although much has been written on borate esters and organoboron compounds very little has been published on organoboron polymers. As a result of this survey an investigation of two general types of boron compounds looked most promising viz. borate esters and alkyl-boranes. Although the borate esters appear to have sufficient

TABLE VI

POLYMERS OFFERING GREATEST PROMISE
AS BASES FOR CASTABLE NEUTRON SHIELD

1. POLYBUTENE EXTENDED BUTYL RUBBER

2. CARBOXY (PENDANT) POLYBUTADIENE – EPOXY

3. DEPOLYMERIZED CIS – 1, 4 POLYISOPRENE

4. DEPOLYMERIZED NATURAL RUBBER

5. CARBOXY POLYBUTADIENE – ALKYL CARBORANE

6. CARBOXY TERMINATED POLYBUTADIENE

7. BORON MODIFIED ACRYLIC ACID TERPOLYMER

3898

oxidative stability many of them are hydrolytically unstable due to the electron deficient boron atom. This tendency to hydrolyze may be overcome by sterically shielding the boron-oxygen bonds with neighboring alkyl or aryl groups. Also, the tendency to hydrolyze should be reduced with increased molecular weight. The alkyl boranes (R_3B), on the other hand, are oxidatively unstable being converted to borate esters or in some cases to the intermediate boronic acid $RB(OH)_2$ [13]. The lower alkylboranes are spontaneously flammable in air, however, the higher members and those which are hindered such as trinaphthyl and trimesityl boranes are much more stable. Decaborane is a relatively stable hydride and derivatives thereof show great stability.[14]

Polymeric borate esters were prepared by several methods as illustrated in Fig. 3. In most cases simple bulk polymerization under inert atmosphere with the last stage consisting of heating under vacuum was satisfactory. A few examples of the types of polyesters prepared are shown in Table VII. The details pertaining to the synthesis of these and others have been described.[15] Although several of these polyborates were castable and elastic, none were considered suitable for the intended application because of sensitivity to oxidation and hydrolysis. Also, due to the oxygen present, the hydrogen densities of polyesters would probably not be at an optimum.

For these reasons, more recent efforts have been concentrated on the preparation of suitable polymers based on alkylboranes or the addition of boranes to existing liquid polymers. The principal synthetic approaches utilized are shown in Fig. 4. The hydroboration reactions shown at the top were used in efforts to incorporate boron into existing liquid polymers. Some examples of the polyorganoboranes which were synthesized are described in Table VIII. The details pertaining to these reactions have been described.[15] The high degree of crosslinking and low boron uptake of the hydroborated polybutadienes makes them unsuitable for shielding.

Among the organoborane polymers studied, the polydiene-decaborane and the copolymers formed from alkenyl carboranes and dienes appear to offer the most promise toward a stable boron elastomer for neutron shielding. The latter system is especially attractive due to the hydrolytic and oxidative stability of the resulting elastomers and the rather low percentage of the carborane component required to yield the boron content desired. Using suitable modifications one could readily

FIGURE 3

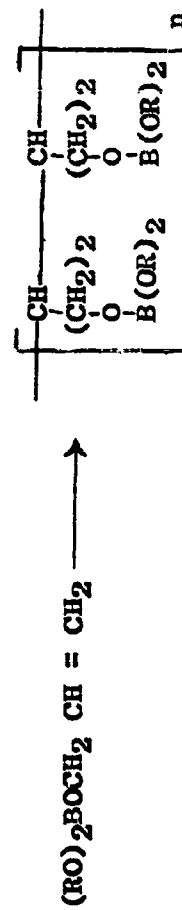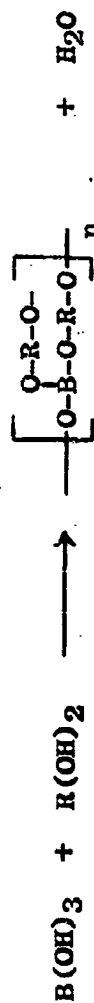### Methods Used For Synthesizing Polymeric Borate Esters

$$RB(OH)_2 \ + \ R'(OH)_2 \ \longrightarrow \ \left[R'-O-\overset{\overset{\textstyle R}{|}}{B}-O-R'-O \right]_n \ + \ H_2O$$

$$RBCl_2 \ + \ R'(OH)_2 \ \longrightarrow \ \left[R'-O-\overset{\overset{\textstyle R}{|}}{B}-O-R'-O \right]_n \ + \ HCl$$

$$(RO)_3B \ + \ R'(OH)_2 \ \longrightarrow \ \left[R'-O-\overset{\overset{\textstyle O-R}{|}}{B}-O-R'-O \right]_n \ + \ ROH$$

$$B(OH)_3 \ + \ R(OH)_2 \ \longrightarrow \ \left[O-\overset{\overset{\textstyle O-R-O}{|}}{B}-O-R-O \right]_n \ + \ H_2O$$

$$HO-R-\theta-R-OH \ + \ R'(CO_2H)_2 \ \longrightarrow \ \left[R-\theta-R-OOC-R'-COO \right]_n \ + \ H_2O$$

$$(RO)_2BOCH_2 \ CH = CH_2 \ \longrightarrow \ \left[\overset{\textstyle CH-}{\underset{\textstyle B(OR)_2}{\underset{\textstyle O-}{\underset{\textstyle (CH_2)_2}{|}}}} \overset{\textstyle CH}{\underset{\textstyle B(OR)_2}{\underset{\textstyle O}{\underset{\textstyle (CH_2)_2}{|}}}} \right]_n$$

247

TABLE VII

Examples of Polyborate Esters Synthesized
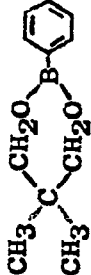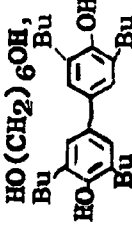
Acid, Ester or Halide	Diol	Catalyst	Nature of Product	Remarks
C₆H₅–BCl_2	$(CH_2OH)_2-C(CH_3)_2$	None		Short chain glycols yield cyclic products
$R-B(OH)_2$ R=Bu, Nonyl, Dodecyl	$HO(CH_2)_6OH$, $HO(CH_2)_{10}OH$	CH_3–C₆H₄–SO_3H	Viscous Polyesters	Degraded to hard mass on standing
C₆H₅–$B(OH)_2$	$HO(CH_2)_6OH$	Sb_2O_3	Viscous, tacky polymer	Converted to semi-solid by H_2O_2
$(C_4H_9O)_3$ B	$HO(CH_2)_6OH$,	None	Resilient, oily, gum	Oxidized on exposure to air

248

TABLE VII (Cont.)

Acid, Ester or Halide	Diol	Catalyst	Nature of Product	Remarks
$B(OH)_3$	CH_3 CH_3 $HO-C-CH-C\equiv C-CH-C-OH$ CH_3 CH_3	None	Hard, sticky, polymer	Oxidized on exposure to air
$R-B(OH)_2$ R=Dodecyl	1,3 Bis [3(2,3 epoxy-propoxy) propyl] tetra-methyl siloxane	None	Gel	Oxidizes in air
$(CH_2)_8(COCl)_2$	HO $CH_2\Theta CH_2OH$	None	Elastic gum	Insol; appears to be cross-linked
$(CH_2=CH\ CH_2)_2B-O-$ Bu(t) Bu(t)	None	(1) Peroxide (2) Ziegler $(C_2H_5)_3Al +$ $TiCl_4$ (3)$AlCl_3$	No polymer formed	–

FIGURE 4

Some Proposed Synthetic Routes To Polyorganoboranes

Reaction	Ref.
$6 \ R\text{-}CH=CH_2 + B_2H_6 \xrightarrow{\text{ether}} 2(RCH_2CH_2)_3 B$	16
$3 \ RCH=CH_2 + \text{Pyridine} : BH_3 \xrightarrow{\Delta} (RCH_2CH_2)_3 B$	16
$Li\text{-}(CH_2\text{-}CH=CH\text{-}CH_2)_n\text{-}Li + BF_3 \cdot Et_2O \longrightarrow Et_2O \cdot BF_2\text{-}(CH_2CH=CH\text{-}CH_2)_n\text{-}BF_2 \cdot Et_2O$	15, 17

$$CH_2=CH\text{-}CH_2 B_{10}H_{12} + CH_3\text{-}\overset{\overset{\textstyle CH_3}{|}}{C}=CH_2 + CH_2=\overset{\overset{\textstyle CH_3}{|}}{C}\text{-}CH=CH_2 \longrightarrow$$

$$\left[\begin{array}{c} CH\text{-} \\ | \\ (CH_2)_2 \\ | \\ B_{10}H_{12} \end{array}\right]_x \left[\begin{array}{c} CH_3 \\ | \\ \text{-}C\text{-}CH_2\text{-} \\ | \\ CH_3 \end{array}\right]_y \left[\begin{array}{c} CH_3 \\ | \\ \text{-}CH_2\text{-}C=CH\text{-}CH_2\text{-} \end{array}\right]_z$$

Ref: —
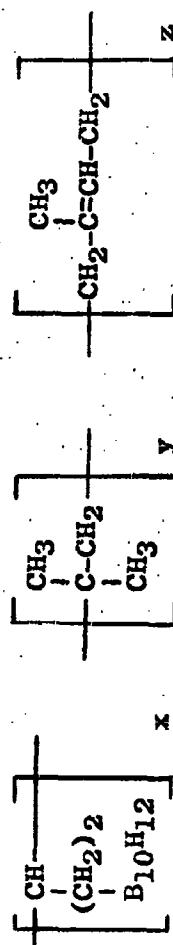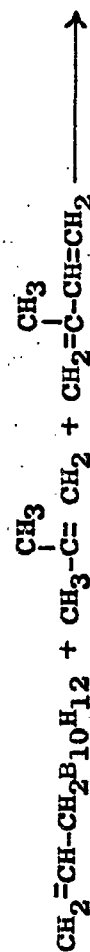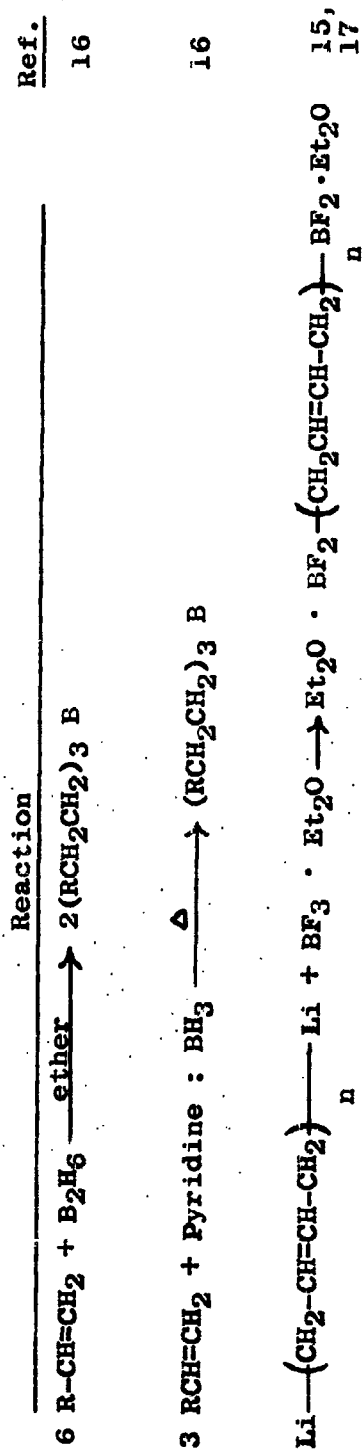
FIGURE 4 (Cont.)

Reaction	Ref.
$C_4H_9 BCl_2 + (BrMg)_2C_4H_8 \longrightarrow \left[C_4H_8 - \overset{\overset{\textstyle C_4H_9}{\mid}}{B} \right]_n$	-
$Li-\left(CH_2-CH=CH-CH_2 \right)_n + B_{10}H_{14} \longrightarrow$	15
$-\left(CH_2-CH=CH-CH_2 \right)_n B_{10}H_{12} \longrightarrow \left(CH_2-CH=CH-CH_2 \cdot B_{10}H_{12} \right)_n$	14
$ROCH=CH_2 + CH_2=CH-CH=CH_2 \longrightarrow \left[\overset{\overset{\textstyle O-R}{\mid}}{CH}-CH_2-CH_2-CH=CH-CH_2 \right]_n$	14

251

TABLE VIII

Examples of Polyorganoboranes Synthesized

"Hydrocarbon" Reactant	"Boron" Reactant	Catalyst	Nature of Product	Remarks
Liquid $\{CH_2CH=CH-CH_2\}_n$	$(C_5H_{11})_3$ B	None	Yellow, crumbly	4.4% Boron
Liquid $\{CH_2-CH=CH-CH_2\}_n$	Pyridine : BH_3	None	White, rubbery crumb	2% Boron
$Li\{CH_2CH=CH-CH_2\}_n Li$	$BF_3 \cdot Et_2O$	None	Viscous liquid	.45% Boron; M.W. (est.) 5,000
$Li\{CH -C(CH_3)=CH-CH_2\}_n Li$	$B(OCH_3)_3$	None	Mobile liquid	4.7% Boron; sensitive to air

TABLE VIII (Cont.)

"Hydrocarbon" Reactant	"Boron" Reactant	Catalyst	Nature of Product	Remarks
Li$-\left(CH_2-CH=CH-CH_2\right)_n$-Li	$B_{10}H_{14}$	None	Solid gum; foamed upon work up	6% Boron
$CH_2=CH-CH=CH_2$ + $CH_3(CH_2)_5CH=CH_2$	B_2H_6	Triglyme	Low boiling alkyl-borane complex	Gave mill-able gum on reaction with polybutadiene 4.4% Boron
$CO_2H\left(CH_2-CH=CH-CH_2\right)_n Cl_2H$	Pyridine : BH_3	Triglyme	Rigid, cellular, very hard	–
$CH_2=CH-CH=CH_2$	$\overset{CH_3}{\underset{\|}{H-e-C=CH_2}}$	Peroxide	Tough elastomer	24% Boron; Hydrolytically oxidatively very stable

253

obtain a series of elastomers having varying boron content for shielding against a wide range of radiation spectra. To aid in curing at room temperature, reactive crosslinking sites such as carboxy or epoxy groups should be incorporated along the chains. In order to improve the hydrogen density, consideration should be given to stereoregular elastomers of this type. These would be expected to have higher specific gravities with essentially the same hydrogen content and consequently greater hydrogen densities.

Conclusions

In conclusion it may be said that the work thus far has pointed to several materials which should be optimized and evaluated for an immediate solution to this problem. Also, several avenues of approach have been uncovered which will be useful in a final solution to this problem.

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DISCUSSION ON RADIATION PROBLEMS - POST CONFERENCE COMMENTS

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The wide diversity in interests exhibited in just four papers points up the fact that radiation effects on elastomers are far too complex to be considered a single problem. In fact, the only common property to be found in "radiation" is the availability of large amounts of energy for absorption by the elastomer. Perhaps the most important thing to remember is that effects depend on the nature of the radiation and are not proportional to the incident time-integrated energy flux. Even the rule-of-thumb that effects are proportional to the total energy absorbed i only a crude approximation.

Electromagnetic radiation, ranging in energy from ultraviolet to hard gamma, contains enough energy per photon to interact with valence electrons and produce ions or free radicals. A high-energy photon generally escapes after depositing only a fraction of its energy by Compton interaction within the elastomer; a low-energy photon is much more likely to be absorbed completely.

Charged particles, such as electrons, protons, alpha particles, and even heavier ions in cosmic rays, produce a dense track of ionization. Interactions with atomic nuclei are rare, as Coulomb forces tend to prevent close approach. Despite the short range of charged particles, the intense ionization is very damaging.

Neutrons are particulate and uncharged; and, in addition to the effects mentioned above, can knock atoms completely out of their molecular and crystalline sites. This process alone is enough to account for the observed fact that in biological systems neutrons are, erg for erg, several times more destructive than gamma rays. Life is based on proteins, macromolecules containing carbon, hydrogen nitrogen, and some oxygen and sulfur; the chains are helical and interweave helically with other chains. It would be difficult to ignore the analogy to elastomers, based on organic polymers with orientation and cross-linking of chains.

Mr. McGarvey and Dr. Pestaner, in their papers, were concerned with effects of gamma radiation on materials. Both the beneficial and detrimental effects were considered, and even though the source of radiation was limited to cobalt-60, a generalized validity can be claimed. Because of the nature of Compton scatter and the fact that the process produces a broad spectrum, different energy gamma rays will behave similarly, providing allowance is made for the unabsorbed energy.

Dr. Miller, interested in a space environment, may have some difficulty in applying her results to either true space conditions or any reasonable terrestrial conditions. Her studies were performed in vacuum and a discrete ultraviolet spectrum from a mercury arc. Her finding that a predominantly cross-link mechanism becomes a chain-scission process at as low as 10^{-4} mm oxygen pressure limits the value of the results to space exposure. Although it is true that the research was directed only toward effects in space, the mercury spectrum is not representative of the wide continuous solar ultraviolet spectrum. Also, although variables must be studied singly, it is probable that ultraviolet represents only a small fraction of the deleterious environment in this part of the solar system. The solar wind, particularly during periods of flare activity, is composed largely of charged particles. This is not a criticism of the work, which was planned to provide valuable information and did so. Rather, the foregoing indicates the direction of further research as exposure to accelerated particles and, eventually, extra-atmospheric conditions. It is suggested that only exposure in deep space and subsequent recovery of specimens can be considered definitive experiments. It is dangerous to extrapolate to conditions which are still poorly known.

Mr. Ossefort has presented some advances in personnel protection against neutrons. When the end use of an elastomer is that of a neutron shield, degradation of physical properties is of no concern. With possible use of polymers in the immediate vicinity of nuclear reactors however, it would be advantageous to protect the materials against neutron damage. Boron is a good absorber of neutrons only after they have lost most of their energy. Unfortunately, it is the hydrogenous polymer which bears the brunt of thermalizing the neutrons, with disruption of the molecule and liberation of high energy protons. Also, absorption of neutrons by any nucleus produces prompt gamma radiation inside the elastomer. Incorporation of hydrogenous additives would help, but it is likely that amounts sufficient to absorb an appreciable fraction of the neutron collision energy would degrade the elastomer's physical properties without any radiation exposure. Antirads and low atomic number fillers should offer the greatest promise in reducing neutron-induced damage.

To summarize, the reported work is of importance and applies within the <u>limitations of the experimental conditions and intended material use.</u> Great care must be exercised in extrapolation whenever radiation is involved. Several needed programs and possible research directions are proposed.

HIGH TEMPERATURE RESISTANT ELASTOMERS

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Several years ago The Firestone Tire and Rubber Company, under contract with the United States Air Force, undertook to measure at elevated temperatures some of the significant physical properties of vulcanized elastomers. All types commercial elastomers were included in this survey as well as a number of experimental polymers (1). Properties measured included tensile strength, elongation, hardness, rebound, permeability and aging resistance. These properties were measured at temperatures as high as 550°F (2).

The present paper includes a brief review of the stress-strain properties of the more heat resistant elastomers at 400°F, presents results of high temperature stress-relaxation studies, and describes some recent fundamental studies involving chromatographic identification of volatile decomposition products evolved during high temperature aging.

Stress-Strain Properties @400°F

The elastomers in widest use, or holding the most immediate promise of use, in applications requiring heat resistance are silicone, fluorocarbon, butyl or chlorinated butyl, and ethylene/propylene (EPR) rubbers. Stress-strain properties of vulcanizates of the above polymers were measured over a range of temperatures; however, the properties measured in air at 400°F were chosen for purposes of comparison. The values shown in Figure 1 are typical values but not necessarily the highest that could be attained by varying compounding techniques. Formulations for all compounds appear in Appendix I.
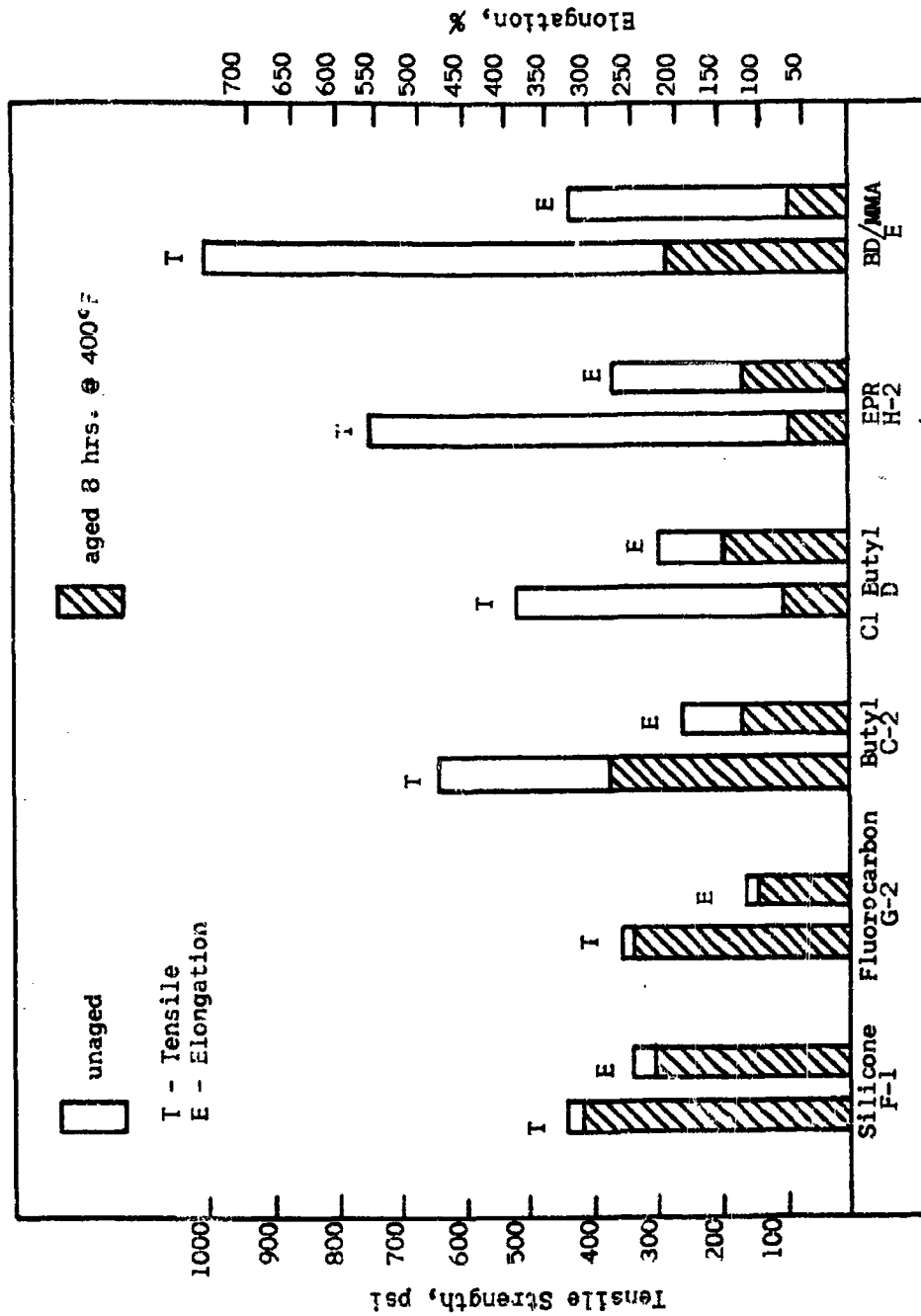
Figure 1. Typical Stress-Strain Values of Vulcanizates at 400°F.

The silicone (F-1) and fluorocarbon (G-2) vulcanizates were postcured at 480 and 400°F respectively and hence show little effect of 8 hours additional aging at 400°F. The butyl compound (C-2) was resin cured and probably represents about the best balance of high temperature strength, aging resistance, and processibility possible for this elastomer. Raising the HAF black level from 50 to 60 phr in this particular compound would raise the initial 400°F tensile approximately 15-20% but processing quality would suffer. Chlorinated butyl (D) can be compounded to have reasonably high initial tensile strength but generally has poorer aging resistance than regular butyl when so compounded. EPR can also be compounded to yield high initial 400°F tensile strength but likewise tends to have poor aging characteristics. Aging resistance can be improved in certain instances by the use of antimony trioxide and hydration (5). The compound shown (H-2) represents a saturated EPR cured with peroxide and sulfur. The newer EPR terpolymers, containing a small amount of unsaturation, have been cured with lower levels of peroxide and sulfur to yield over 800 psi tensile strength at 400°F. Better aging resistance also was obtained with this compound.

As a point of interest, a butadiene/methylmethacrylate cured compound (BD/MMA) was included on the bar graph of Figure ___ polymer has been compounded to have tensile strength as ___ This 1800 psi at 400°F by curing with Ba(OH)$_2$·8H$_2$O and a ___ high as such a stock is dry and somewhat difficult to proc___ peroxide; however plasticizers to get a more processible stock r___ ss. Addition of tensile strength. T___ BD/MMA (D) stock ages ___ uces the maximum coming brittle in as little as 4 hours. ___ poorly at 400°F, be-

Stress Relaxation of Elastomeric Vul___anizates

A second method of evaluat___ng the usefulness of vulcanizates for certain applications is ___ measure their stress relaxation rates at elevated temperatures. ___ Measurement of stress relaxation is now an accepted method of d___ ermining the resistance of a polymer to thermal deterioration ___ its structure, the results being interpreted in terms of the rates ___ relaxation of both primary and secondary chemical bonds.

The tests ___ ere conducted according to the techniques described in a paper by ___ obolsky, Prettyman and Dillon (4). Initial stress decay is be___ eved to be due to the relaxing of the secondary network attraction ___ and to the uncoiling of some polymer chains. The larger amount ___ s stress decay is attributed to oxidative scission of bonds al___ f the molecular chains or at network junctures. Spontaneous ___ the rupture may occur also at or adjacent to vulcanization cross-links.

The apparatus used was the same as that used by Tobolsky, et al. with modifications to permit testing at temperatures up to

261

350°F. This apparatus c̲ ... ̲
operating against the ̲ ̲ ̲ ̲ sts ̲ ̲ ̲ ̲ ̲ ̲ ally of a special ̲ ̲ am balance
Comparisons were ̲ ̲ ̲ ̲ ̲ rce of a ̲ ̲ ̲ ̲ ̲ ated band of the vulc̲ ̲ ̲ ̲ ̲ .
stress measu̲ ̲ ̲ ̲ ̲ de of the ti̲ ̲ requi̲ ed to relax 63.2% of the
̲ ̲ ̲ ̲ ̲ o̲ ̲ half minute after the start of the test.

The first series of tests included vulcanizates of the more
̲ ̲ dely used elastomers as well as those of the more heat resistant
polymers. A wide range of relaxation times were obtained and are
recorded in Table 1. The posture given the silicone and fluoro-
carbon stocks contribute to their excellent resistance to stress
decay as evidenced by the more than 10,000 and 7500 minutes respect-
ively required to relax the standard 63.2% of one-half minute stress.
By comparison, all other stocks had rapid stress decay rates at this
temperature; therefore subsequent tests were made at 300°F.

TABLE 1

CONTINUOUS STRESS RELAXATION OF SIX ELASTOMERS AT 350°F

Measured at 50% extension

Feature	Time to Relax 63.2% of 0.5 Minute Stress, Minutes
Silicone (F-1)	over 10,000
Viton A-HV (G-1)	7,500
Butyl (C-1)	80
BD/MMA (E)	66
SBR (B)	10
Hevea (A)	9

Continuous stress relaxation values at 300°F are shown in
Figure 2 for silicone, fluorocarbon, resin cured butyl and EPR
vulcanizates. Again it is shown that the silicone and fluorocarbon
compounds had the lowest rates of chain scission (decrease in stress).
Stress decay in the EPR vulcanizate was more rapid than in the butyl
compound for the first 100 minutes but the two were equal thereafter.

Judging from stress relaxation rates only, the vulcanizates
would rank for heat resistance in the order of silicone, fluorocarbon,
butyl, and EPR.

Chromatographic Analysis of Volatile Decomposition Products

The foregoing examples are indicative of data that have been
collected in early phases of this program. A few months ago a new
and different technique for measuring the inherent thermal stability
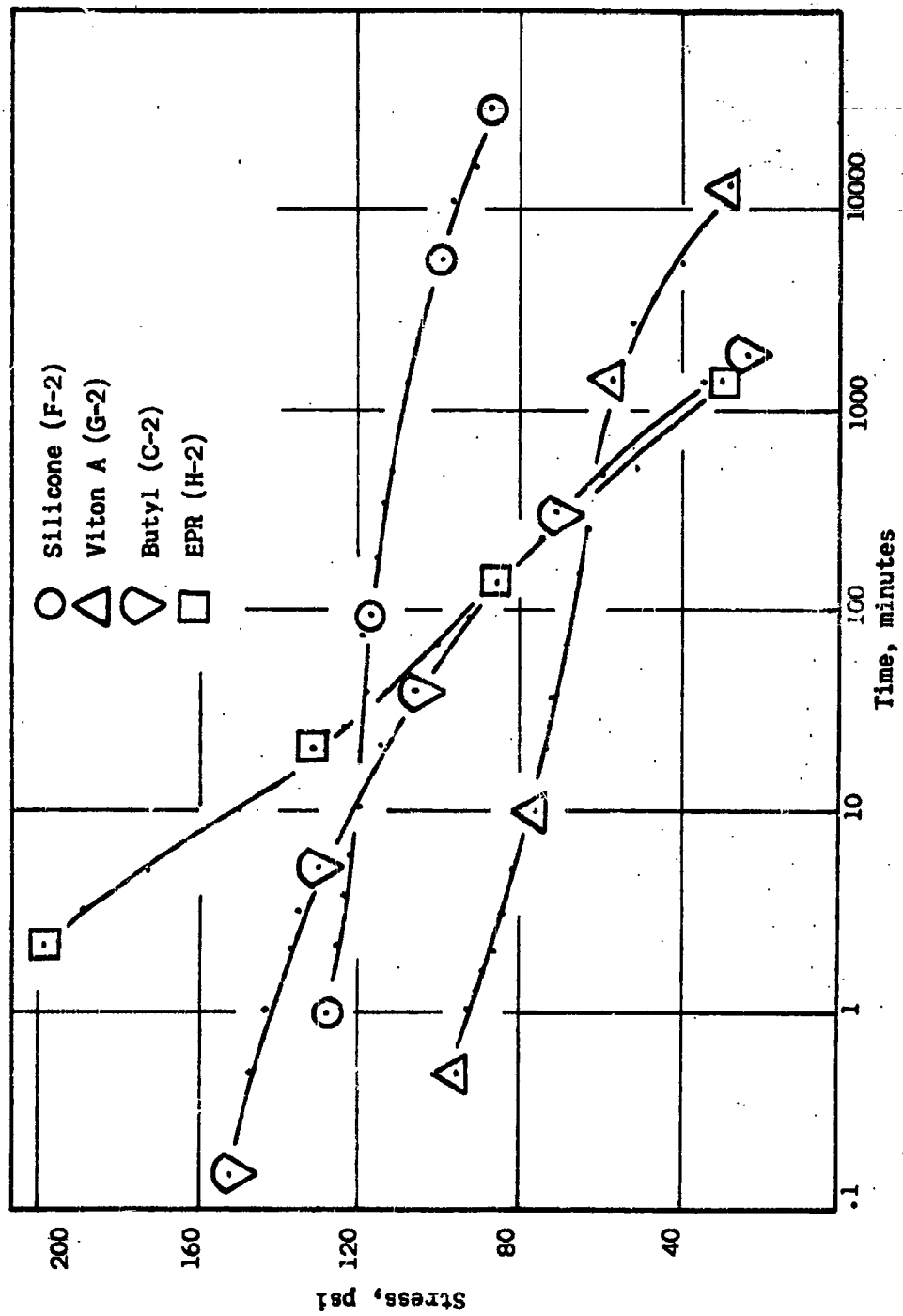of elastomeric compounds was devised which utilizes a modified high

Figure 2. Continuous Stress Relaxation of High-Temperature Elastomers at 300°F. Measured @ 50% elongation.

263

temperature chromatograph. This is a more fundamental study of the nature of degradation of elastomers or their compounds in which attempts are made to identify the volatile decomposition products evolved during high temperature aging. The ultimate objective of such a study is to determine the mechanism of thermal decomposition of both elastomers and their vulcanizates and to utilize the information in the production of more heat resistant compounds.

Two different high temperature aging techniques have been studied thus far and they appear to provide a satisfactory means of producing decomposition products for identification. These techniques are: (1) static aging at elevated temperatures in sealed tubes and (2) programmed temperature aging in a dynamic inert gas atmosphere. The volatile products formed under these two aging conditions were analyzed by means of gas chromatography. Detailed analysis of the decomposition products identified after static aging are given for resin cured butyl rubber and peroxide/sulfur cured EPR rubber. Programmed temperature aging data are given for silicone, butyl, EPR, BD/MMA and Viton A compounds. The object of future work will be to identify the decomposition products obtained from a variety of high temperature elastomers and their compounds using the aging conditions and analytical techniques described.

Static Aging of Elastomer Compounds

Static aging of vulcanizates was accomplished by heating samples at various temperatures in specially designed glass tubes. Generally a 2 ml. gas sample was taken by pipette for analysis in chromatographs, using different columns in order to obtain a complete analysis of the products formed.

Vulcanizates of Butyl (C-3) and EPR (H-2) rubbers were aged 14-16 hours at 300, 400, and 500°F and the decomposition products evolved at the various temperatures were identified as shown in Table 2. The conditions used in the chromatographic analysis are also given in Table 2.

At 300°F only oxygen, nitrogen (absorbed air) and a small amount of carbon dioxide are evolved from both butyl and EPR. At 400°F isobutylene appears in the decomposition products from both; diisobutylene and methane also appeared in the volatiles from butyl and EPR respectively. At 500°F isobutane and n-butane were identified in the volatile decomposition products of the butyl compound. The unknown product listed under the EPR heading was traced to compounding ingredients but was never identified.

Having identified the decomposition products qualitatively, a more detailed quantitative analysis of the products formed during 14 hours aging of butyl and EPR compounds at 500°F was made and the

TABLE 2

STATIC AGING OF BUTYL AND EPR AT DIFFERENT TEMPERATURES

Products Identified*

Stock	Butyl (C-3)	EPR (H-2)
Temperature		
300°F	O_2, N_2, CO_2	O_2, N_2, CO_2 Unknown product
400°F	O_2, N_2, CO_2 Isobutylene Diisobutylene	O_2, N_2, CH_4 Unknown product Isobutylene
500°F	O_2, N_2, CH_4, CO_2 Isobutane n-butane Isobutylene Diisobutylene	N_2, O_2, CH_4 Unknown product Isobutylene

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* The amount of volatile hydrocarbon products increased as the aging temperature increased.

Instrument: F and M High Temperature Chromatograph
Column: 14 ft 30% DMS on C22 firebrick
Temperature: 25°C
Gas flow: 25-40 ml/minute.

results are shown in Table 3. It is seen that the major portion of the volatile product produced by both rubber samples consists of nitrogen and oxygen. Since the sample tubes were flushed with nitrogen and evacuated before heating, this indicates that the samples contained a considerable amount of absorbed nitrogen and oxygen (air). This absorbed oxygen is capable of causing oxidation at elevated temperature even in an inert atmosphere. Such oxidation is probably the source of the CO_2 identified in the volatile products. In this analysis methane was identified as a product of both polymers, and a trace of propane was found in the decomposition products of EPR. Neither ethylene nor propylene have been detected in volatile products from EPR.

It should be noted that the butyl stock produced about three times as much volatile hydrocarbon product as the EPR stock and that the butyl test strips were more degraded than the EPR strips. Considering this evidence one would conclude that the EPR compound was more stable than the butyl compound under these static aging conditions at 500°F.

Programmed Temperature Aging of Elastomer Compounds

The equipment used for programmed temperature aging of samples in a dynamic inert gas atmosphere was a modified F and M Model 500 High Temperature Chromatograph. Modification consisted of replacing the usual gas chromatographic column with an aging cell. At the start of each test the system was brought to equilibrium at 50°C. Programmed heating of the sample was scheduled at a rate of 5.6°C/minute.

The volatile products formed during the aging period were swept along by the carrier gas (helium) and measured collectively by a thermoconductivity cell. The results were recorded on a strip chart recorder. Samples of the volatile products were collected with a volumetric pipette from the exhaust port of the F and M Chromatograph at various temperature ranges and analyzed on a Fisher-Gulf Partitioner. Data which have been obtained from such studies on vulcanizates of five elastomers are shown in Figures 3 and 4. The vertical axis of the figures represents the recorder deflection produced by volatile decomposition products flowing through the detector cell. Time is measured on the horizontal axis and can be converted to temperature by multiplying by 5.6°C/minute and adding 50°C for the equilibrium starting temperature.

It will be observed that although some volatile materials are evolved in the early stages, each sample reached a temperature at which there was a rapid evolution of volatile products. The relative decomposition temperature for each compound has been chosen arbitrarily as the point during the rapid decomposition stage where the recorder shows 50% deflection. The relative decomposition

266

TABLE 3

VOLATILE PRODUCTS IDENTIFIED FROM STATIC AGING OF BUTYL AND EPR COMPOUNDS

Aging Period: 14 hours at 500°F

Component, %	O_2	N_2	CH_4	CO_2	Isobutane	n-Butane	Isobutylene	Diisobutylene
Butyl (C-3)*	13.9	78.4	2.9	2.9	0.20	0.20	1.30	0.20

Component, %	O_2	N_2	CH_4	CO_2	Propane	unknown Component	Isobutylene	C_5-C_{10}
EPR (H-2)	12.8	83.6	1.1	2.17	0.13	0.10	0.02	0.07

* Traces of heavy hydrocarbons in the C_5-C_{10} range were also observed.
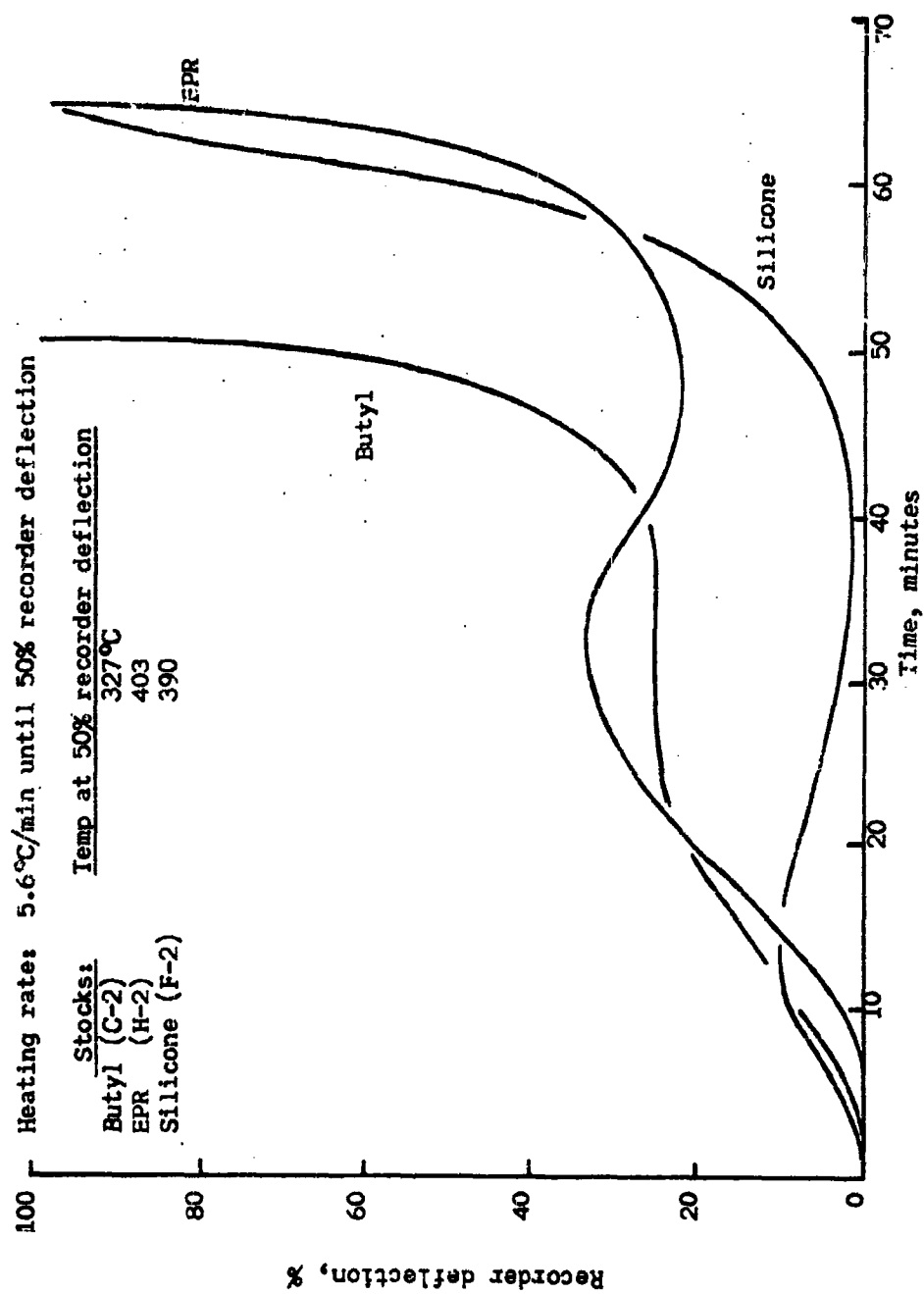
Figure 3. Programmed Temperature Aging of Cured Butyl, Silicone and EPR Stocks

Heating rate: 5.6°C/min until 50% recorder deflection

Stocks:	Temp at 50% recorder deflection
Viton A (G-2)	340°C
BD/MMA (E)	286

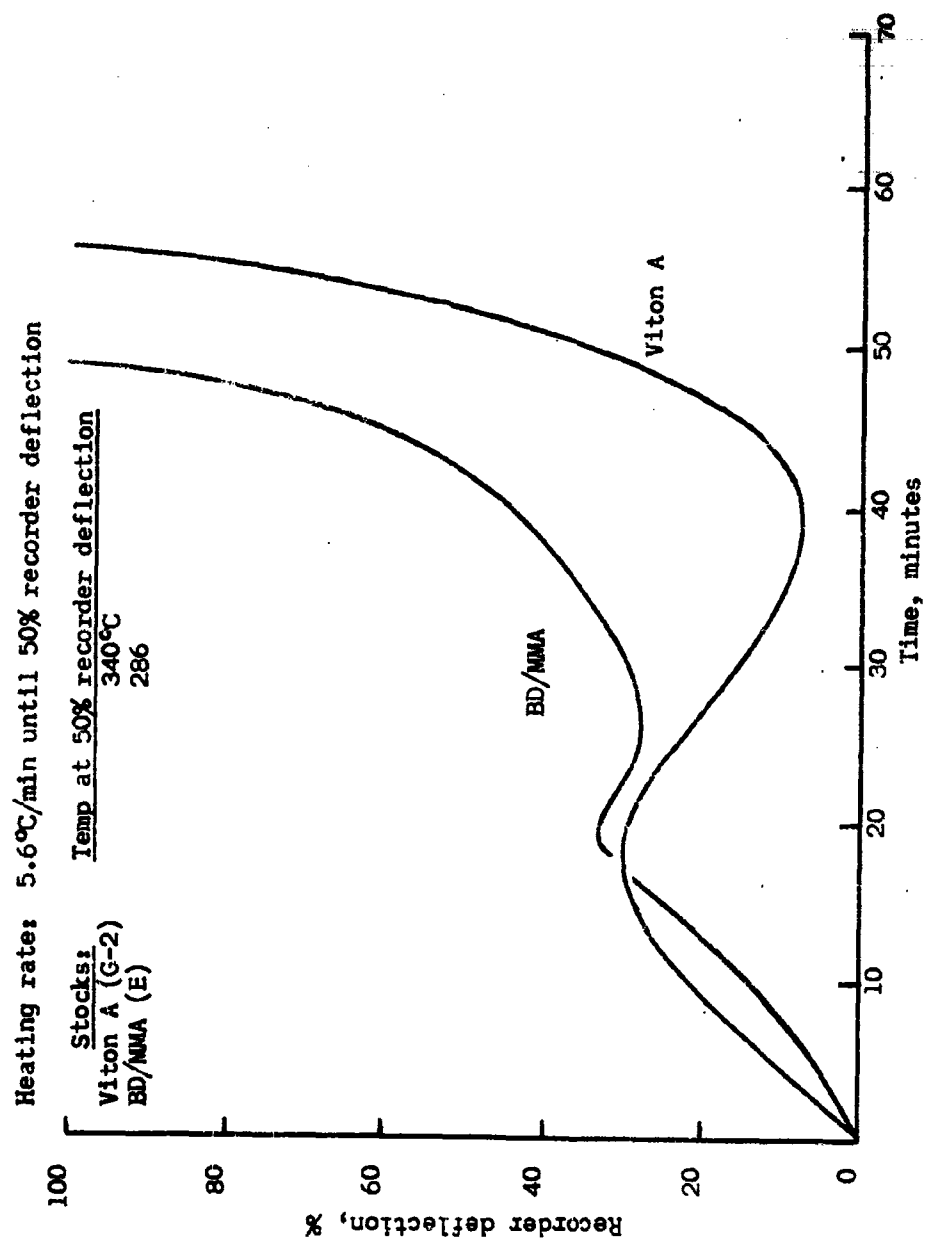Recorder deflection, %

Time, minutes

Viton A

BD/MMA

Figure 4. Programmed Temperature Aging of Cured Viton A and BD/MMA stocks

269

temperatures for the EPR, silicone and butyl compounds were 403, 390, and 327°C respectively (Figure 3). The corresponding temperatures for Viton A and BD/MMA compounds were 340 and 286°C respectively (Figure 4). These decomposition temperatures are recorded with the appropriate curves in Figures 3 and 4. From these data and under these aging conditions, peroxide/sulfur cured EPR was slightly better than the silicone compound and had the greatest inherent heat stability of all the elastomeric compounds studied. This contrasts sharply with the data shown in Figure 1 in which the EPR compound showed evidence of considerably greater loss in properties than either the silicone or butyl compounds when aged in air for a longer period at a much lower temperature (8 hours @400°F). The sweeping action of the inert gas in removing decomposition products is evidently beneficial to the aging of EPR, since these results indicate that gross decomposition of the elastomer during programmed aging in an inert atmosphere does not occur until substantially higher temperatures are reached (400°C). It is theorized that loss of physical properties at lower temperatures is the result of broken crosslinks induced by vulcanization. The breaking or reforming of crosslinks would cause very little evolution of gases. On the other hand the rapid evolution of volatile products noted can come only from polymer decomposition. Therefore this test should be considered as a means of evaluating polymer stability rather than crosslinked network stability.

In order to understand the programmed temperature aging curves better, an attempt was made to identify the volatile materials produced during the aging of two compounds -- butyl and EPR. Samples were collected at regular intervals during the programmed temperature run and were analyzed on a Fisher-Gulf Partitioner. The results were significant and are summarized in Figures 5 and 6 which represent the programmed aging curves of butyl and EPR respectively. The identification of the volatile products are shown opposite the temperatures at which the gas samples were taken. The discontinuities in the curves mark the temperature ranges during which samples were taken for chromatography.

It is seen that from the butyl compound (C-3) only oxygen and nitrogen could be detected in the volatile products evolved at 100-110°C and 200-210°C. The sample collected at 300-310°C just prior to the elastomer decomposition point contained CO_2 (attributed to oxidation) and gave the first evidence of any hydrocarbon decomposition products. The last sample collected after the recorder had gone off scale (indicating rapid elastomer decomposition) showed the presence of considerable hydrocarbon decomposition products above the C_4 range.

During the aging of the EPR compound (H-1), all samples collected before 350°C contained only oxygen, nitrogen and CO_2
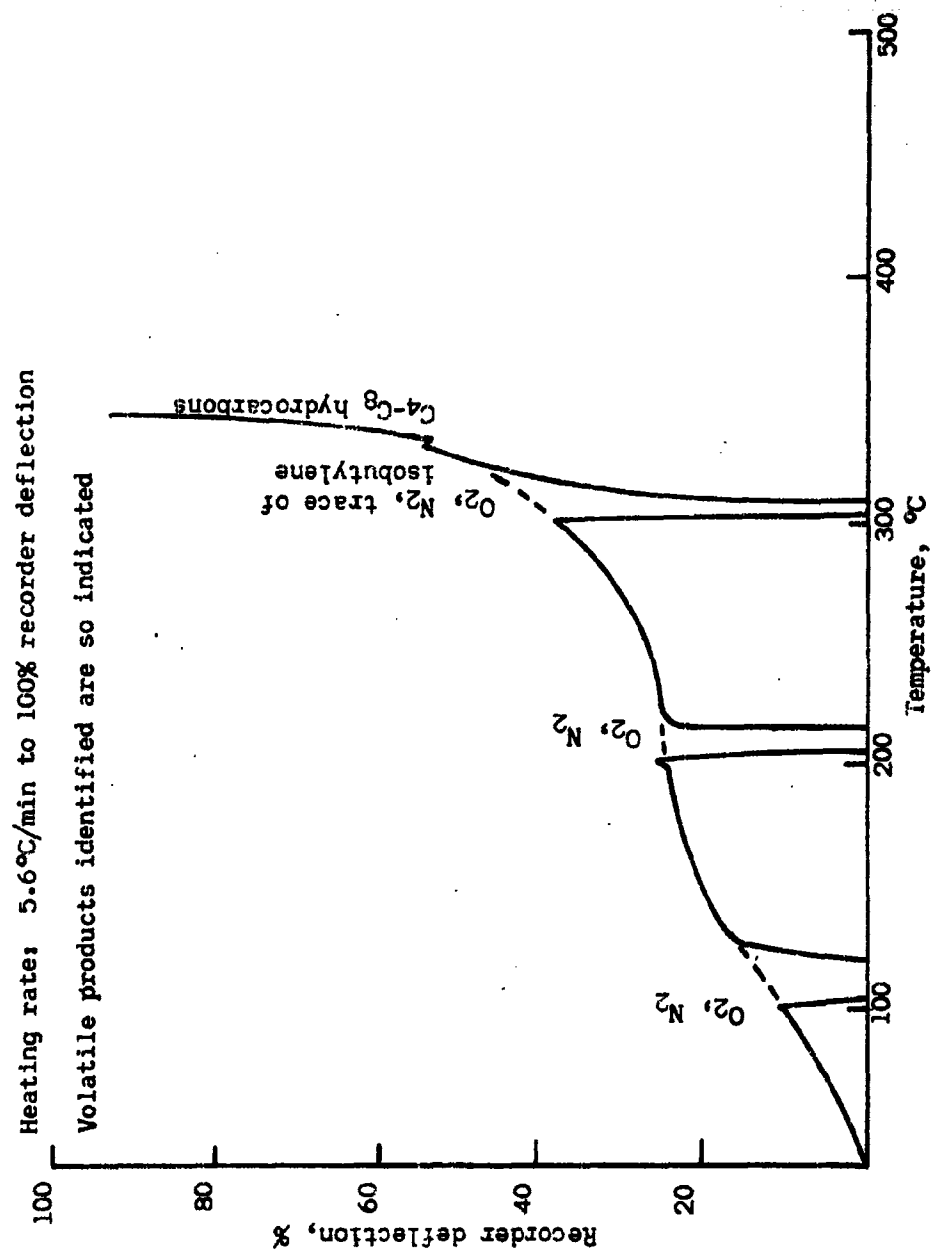
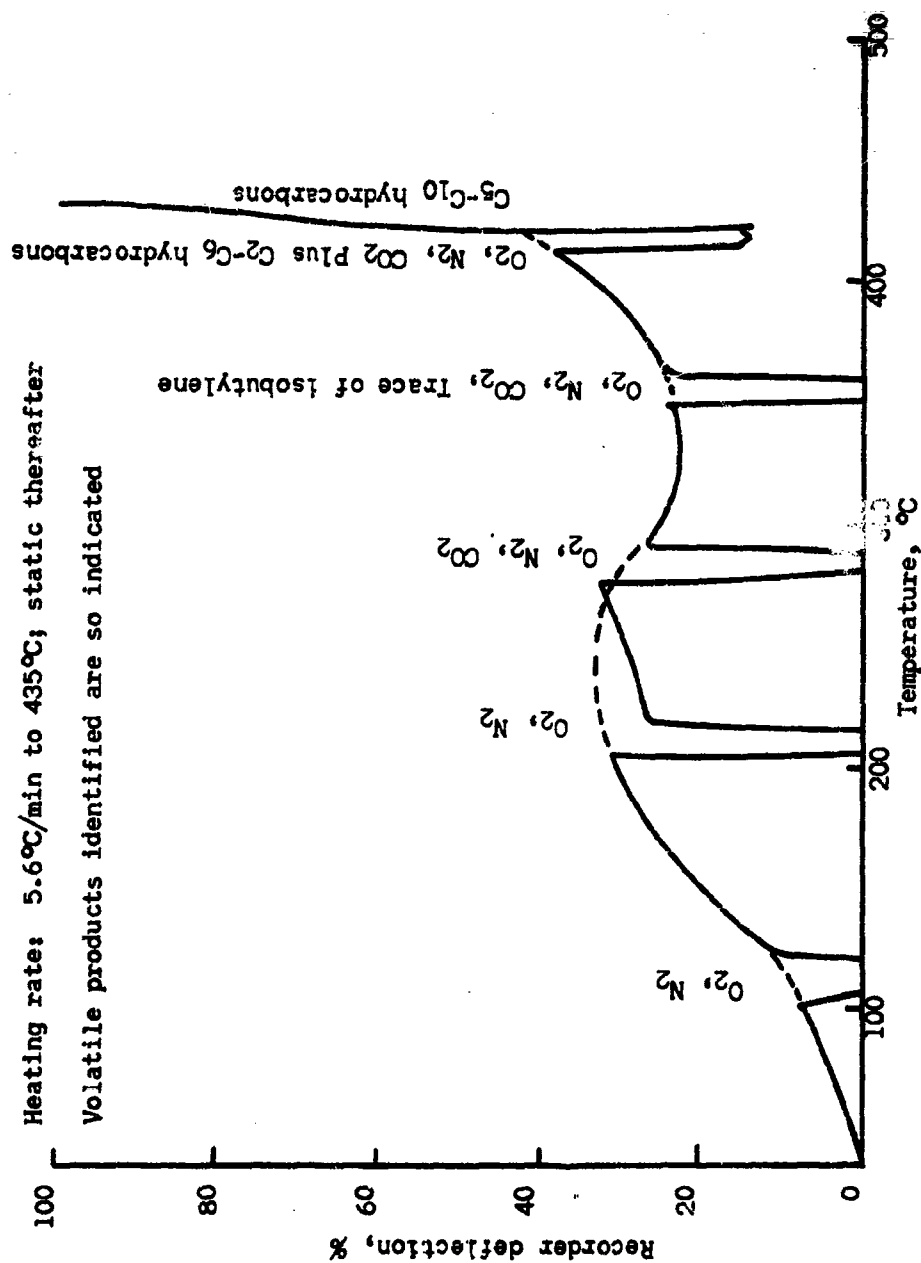Figure 5. Programmed Temperature Aging of Cured Butyl Stock C-3

Figure 6. Programmed Temperature Aging of Cured EPR Stock H-1

Heating rate: 5.6°C/min to 435°C; static thereafter

Volatile products identified are so indicated

(Figure 6). Hydrocarbon products began to appear immediately prior to elastomer decomposition at 400-410°C. Again considerable hydrocarbon products were found in the sample collected after the recorder had gone off scale.

These results show that the volatile products evolved before the elastomer decomposition point consist mainly of oxygen, nitrogen, and small amounts of CO_2. This may explain why cured elastomers appear to exhibit better aging characteristics in a dynamic inert gas atmosphere than in air. Slowly raising the temperature and flushing the sample chamber with an inert gas appears to remove the absorbed oxygen from the sample to provide better aging performance. The physical characteristics of the samples resulting from programmed temperature aging in helium differed from those aged in air. The resin cured butyl and peroxide/sulfur cured EPR soften in helium but have surface resinification when aged in air. The BD/MMA compound became hard and brittle in both helium and air. Silicone and Viton compounds were little affected by either type of aging, although the silicone stock did exhibit lower elongation after the dynamic aging in helium.

Summary

Stress-strain properties at 400°F, stress relaxation properties at 300-350°F, and a decomposition temperature associated with programmed heat aging in a dynamic inert atmosphere have been used as criteria for evaluating the heat resistance of selected vulcanizates, including those of silicone, fluorocarbon, butyl and ethylene/propylene rubbers. It was shown that these elastomeric compounds may vary in their ranking as heat resistant materials depending upon the test involved. For example, the EPR compound ranked very low in the stress relaxation test, but ranked highest for decomposition temperature during programmed aging in an inert atmosphere.

The relative decomposition temperatures were arbitrarily selected as the points, during the rapid evolution of volatile products, where the recorder showed 50% deflection. For the vulcanizates of EPR, silicone, Viton A, and butyl rubber the decomposition temperatures were 403, 390, 340 and 327°C respectively.

Identification of volatile decomposition products evolved during static and dynamic aging in inert atmospheres was undertaken for butyl and EPR compounds as a first step toward a better understanding of the decomposition processes involved. Volatile products collected during the static aging of a butyl compound were identified as nitrogen, oxygen, methane, carbon dioxide, isobutane, n-butane, isobutylene and diisobutylene. Volatiles produced during the static aging of EPR were nitrogen, oxygen, methane, carbon dioxide, propane, isobutylene, and C_5-C_{10} hydrocarbons. Similar identification of

decomposition products is planned for silicone and fluorocarbon compounds.

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APPENDIX I. COMPOUNDING RECIPES

A. Hevea

Smoked Sheet	100
HAF black	50
Zinc oxide	3
Stearic acid	3
Pine tar	3
Antioxidant	1.6
Sulfur	2.6
Santocure	0.5

Cure: 60/280°F

B. SBR (LTP)

FR-S 1500	100
HAF black	50
Zinc oxide	3
Stearic acid	2
Antioxidant	0.6
Processing oil	8
Sulfur	2.0
Santocure	1.2

Cure: 60/280°F

C-1. Butyl Rubber

Enjay Butyl 325	98
Hycar 2202	2
HAF black	60
Stearic acid	1
Amberol ST-137	12

Cure: 90/320°F

C-2. Butyl Rubber

Enjay Butyl 268	100
HAF black	50
Zinc oxide	5
Zinc stearate	3
Processing oil	3
Amberol ST-137	12
$SnCl_2 \cdot 2H_2O$	1

Cure: 60/320°F

C-3. Butyl Rubber

Enjay Butyl 218	100
HAF black	50
Zinc oxide	3.5
Stearic acid	2
Magnesium oxide	1.5
Staybellite Resin	5
Amberol ST-137	12
$SnCl_2 \cdot 2H_2O$	1

Cure: 40/340°F

D. Chlorinated Butyl

Enjay HT 10-66	100
SAF black	50
Zinc oxide	5
Stearic acid	1
Amberol ST-137	5
Sulfur	1.5
MBTS	1
Tellurac	1

Cure: 60/310°F

275

APPENDIX I (CONT'D)

E. Methacrylate Rubber

BD/MMA	100
HAF black	30
Pine tar	5
Antioxidant	2
Di-Cup 40C	3
$Ba(OH)_2 \cdot 8H_2O$	15

Cure: 45/320°F

F-2. Silicone Rubber

Silastic 916 U	100
Di-t-butyl peroxide (20%)	3.5

Press Cure: 20/300°F
Postcure: 2 hours @300°F
2 hours @350°F
4 hours @400°F
4 hours @450°F
8 hours @480°F

G-2. Fluorocarbon Rubber

Viton A	100
MT black	30
Magnesium Oxide	15
Diak #3	2

Press Cure: 60/300°F
Postcure: 1 hour each @212, 250, 300, and 350°F plus 24 hours @400°F

H-2. EPR

AviSun EPR 40	100
HAF black	60
Agerite Resin D	0.5
Sulfur	1
Di-Cup 40C	10

F-1. Silicone Rubber

SE 555 U	100
Di-t-butyl peroxide (20%)	3.5

Press Cure: 20/300°F
Postcure: 2 hours @300°F
2 hours @350°F
4 hours @400°F
4 hours @450°F
8 hours @480°F

G-1. Fluorocarbon Rubber

Viton A-HV	100
MT black	20
Magnesium oxide	15
Diak #2	0.85

Press Cure: 60/300°F
Postcure: 1 hour each @212, 250, 300, and 350°F plus 24 hours @400°F

H-1. EPR

AviSun EPR 40	100
HAF black	60
Sulfur	1
Di-Cup 40C	10

Cure: 50/310°F

Cure: 50/310°F